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# Quantifying the effect of extractives from mountain pine beetle-attacked lodgepole pine for pulp and papermaking

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## Abstract

The pulping of mountain pine beetle-killed wood can impact tall oil recovery, and severe foaming events exist. These effects may be related to changes in the levels and profiles of extractives in beetle-killed wood. This report summarizes existing knowledge regarding the influence of mountain pine beetle attack on extractives. It expands on this knowledge by using PLS-DA modeling to follow changes in extractives profiles with unattacked-green, red and grey stage woods. Result show that red stage pine has lower levels of glycerides and pimaric acid, but higher levels of sterols, than unattacked green wood. Grey stage woods have extractives profiles that are comparable to unattacked wood, likely due to the biodegradation of glycerides or to abiotic effects. While extractives are implicated in the foaming tendency of TMP pressates and black liquors from beetle-infested wood, other factors related to wood chemistry are just as important when addressing the foaming issue.



Keywords: mountain pine beetle, lodgepole pine, extractives, sterols, glycerdies, resin acids, foam, black liquor, TMP pressates



## Résumé

La transformation en pâte du bois des arbres tués par le dendroctone du pin ponderosa peut avoir des effets sur la récupération de tallöl et crée des incidents importants de spumescence. Ces effets peuvent être liés à des changements dans les quantités et les profils des matières extractibles dans le bois des arbres tués par le dendroctone. Le présent rapport résume les connaissances actuelles concernant l'influence des attaques du dendroctone du pin ponderosa sur les matières extractibles. Il élargit ces connaissances en utilisant un modèle PLS-DA (analyse discriminante partielle par les moindres carrés) afin de surveiller les changements dans les profils des matières extractibles pour le bois non infesté vert et celui aux stades rouge et gris. Les résultats démontrent que le pin au stade rouge présente des taux inférieurs de glycérides et d'acide pimarique, mais un taux supérieur de stérols par rapport au bois vert non infesté. Le bois au stade gris présente des profils de matières extractibles comparables à ceux du bois non infesté, probablement en raison de la biodégradation des glycérides ou d'effets abiotiques. Bien que les matières extractibles aient un rôle à jouer dans la tendance à la spumescence des pressats et des liqueurs noires de PTM provenant du bois infesté par le dendroctone, d'autres facteurs liés à la sylvichimie sont tout aussi importants dans la résolution du problème de spumescence.

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# 1 Introduction

British Columbia is currently experiencing the biggest recorded outbreak of mountain pine beetles in western Canada. Aerial overview data from 2006 showed 9.2 million hectares of BC's pine forests being affected at the red attack stage. As of fall 2006, the volume of attacked timber was estimated at over 450 million cubic metres, including green, red and grey stage wood [1]. Projections are for the beetles to have killed 80% of the standing lodgepole pine in BC by 2013. Adding to the severity of the problem, beetles have managed to cross the Rocky Mountains and moved into Alberta, threatening the jack pine forests of Alberta, which can also serve as a host for the beetle [2]. The mountain pine beetle (*Dendroctonus ponderosae* Hopk.) is a persistent pest of lodgepole pine that prefers to invade mature lodgepole pines; however there is strong evidence that during a widespread epidemic like the current one, juvenile trees are attacked as well [3].

The provincial response has been to encourage the harvesting of infested trees in early (green or red) stages of infestation in order to maximize value recovery from lumber. This has resulted in a large increase in the proportion of mountain pine beetle-infested pine that is being used by BC pulp mills. This, in turn, has resulted in problems associated with the high resin levels typical of pines which have been further aggravated by the resinous response of lodgepole pine trees to beetle infestation. These problems are mill-specific and range from the expected pitch-related issues to problems with tall oil recovery and excessive foaming during the pulping. While extractives have been implicated and are the likely culprit, anecdotal evidence suggests that the nature of the problems warrant further investigation. This study looks at the effects of attack stage and site on the extractives profiles of mountain pine beetle-infested lodgepole pine from the interior of BC.

The change in extractives content and composition can have profound impacts on pulp and papermaking processes when salvaged beetle-killed wood is used. In the pulp mill, recovery of tall oil and other by-products obviously depends on the incoming extractives. A drop in extractives content causes a decrease in these recovered by-products, and thus presents an economical impact for the mill. Such a drop in tall oil is currently seen in many mills in BC, but questions remain regarding the impact of beetle-killed wood utilization on by-product recovery. For example, anecdotal evidence suggests that tall oil production increases with the use of red attack wood, but decreases dramatically once grey stage wood replaces red stage wood, in some cases to zero. A change in extractives content with increasing time-since-death could explain a drop in tall oil production, but no dramatic decrease in extractives content has been confirmed yet. In a recent study [4], large variations in extractives content for pine trees from different biogeoclimatic zones and within each stand were found, but the time-since-death of mountain pine beetle-killed wood seemed to have little influence, thus even with the utilization of advanced grey stage pine there should still be some production of tall oil. The discrepancy between these two observations thus suggests that not only the total amount of extractives, but also the extractives composition or other related changes in the wood are affecting tall oil production.

From the perspective of BC's pulp and paper industry, an increase in extractives levels will influence the pulping process and can be problematic. For example, increases in extractives can result in elevated levels of pitch throughout the mill and in the pulp product, and there can be issues related to the recovery system with kraft mills. These issues have been recently addressed in another report [5]. Many mills that use mountain pine beetle-killed wood experience serious foaming problems. Excessive foaming of brownstock influences the washing efficiency and thus needs to be controlled. Excessive foaming in the paper mill or effluent treatment also leads to a variety of problems. The increased foaming tendency that is observed is likely, at least in part, a result of the changes in extractives content and composition.

Wood extractives are implicated with many problems in both chemical and mechanical pulping, papermaking and effluent treatment. However, many of these problems are mill-specific and are beyond the scope of this study. A mill-specific survey of extractives-related issues has been prepared that highlights some of these issues associated with extractives and BC pulp mills that are dealing with mountain pine beetle-infested wood [5]. This study focuses on i) a survey of extractives in mountain pine beetle-infested pines from the BC interior and ii) the effects of extractives on the foaming propensity of TMP pressates as well as weak black liquors generated during the kraft pulping of these types of woods. The effect of mountain pine beetle time-since-death on extractives profiles will be evaluated and a possible use of these compounds as indicators of time-since-death will be presented. Furthermore, the role of extractives on the foaming issues that have been reported during the pulping of mountain pine beetle-infested wood will be explored.

In the following, a literature review first summarizes the current knowledge of changes in extractives content and composition of wood related to mountain pine beetle infestation and discusses how extractives can affect foaming in mill liquor and effluent streams. The effects of beetle infestation and time-since-death on extractives profiles, and how foaming tendency is affected by pulping beetle-killed wood are then explored in the experimental part of this work, and discussed.

## 1.1 Literature Review

### *1.1.1 Tree Response to Beetle Infestation*

The mountain pine beetle (*Dendroctonus ponderosae* Hopk.) is a persistent pest of lodgepole pine that prefers to invade mature lodgepole pines. The beetles attack trees during summer and females, who attack first, bore under the bark and build their egg galleries in the phloem. They then are joined by a male, and after proliferation the beetles die. Larvae develop and overwinter under the bark where they feed on phloem. They transform into pupae and by the next summer into adults. In late summer, they emerge and attack a new tree thus completing the lifecycle [6]. In cold areas, brood development can take place over the course of two years.

The beetles carry fungal spores picked up during maturation feeding prior to emerging from a tree. When attacking a new tree, spores are introduced into the living tissue and fungi start invading the tree. There are six species of blue-stain fungi associated with mountain pine beetle [7-15]. Two of these, *Ophiostoma clavigerum* (Robins.-Jeff. & Davids) Harrington and *Ophiostoma montium* (Rumb.) von Arx, are consistently isolated from the beetle and from beetle-attacked trees [8,12,14-16]. Of these two, *O. clavigerum* (also known as *Europhium clavigerum* or *Ceratocystis clavigera*) has been shown to be the more aggressive, and causes high mortality [13,16,17]. The high pathogenicity of *O. clavigerum* manifests itself in a large body of literature devoted to the fungus and its influence on lodgepole pine.

Tree response to beetle and fungal attack is twofold, an initial response that occurs upon wounding by the beetle followed by a secondary resinosis. The first response is a release of preformed oleoresins from damaged resin canals that flows out to the site of attack. During secondary resinosis, parenchyma cells around the site of attack produce resinous compounds *de novo* [13, 20]. The combined response results in the "pitch tubes" noted during beetle infestation (Figure 1). These are strong indicators of beetle infestation in a lodgepole pine stem. If the secondary response is effective, the beetle and associated fungi do not establish themselves in the tree [12, 20-22]. However, where secondary resinosis is unsuccessful [12], the tree will be colonized and death ensures. The response of the tree and the action of the fungi result in changes in the extractives content and composition. In general, it can be assumed that at the time of attack and shortly thereafter, the extractives content increases due to secondary resinosis. However, after tree death, biological and chemical activities continue to influence the extractives profiles within a tree.

From the perspective of wood quality, trees that have been infested by mountain pine beetle but still retain green foliage (typically within 1 year of infestation) are said to be in the "green" stage of infestation. Trees that have been killed by the beetle but have retained their needles (typically 2-3 years after infestation) are said to be in the "red" stage of infestation, reflecting the red colour of the needles. After 3 years, the dead, standing trees have lost their needles and are said to be in the "grey" stage of infestation.

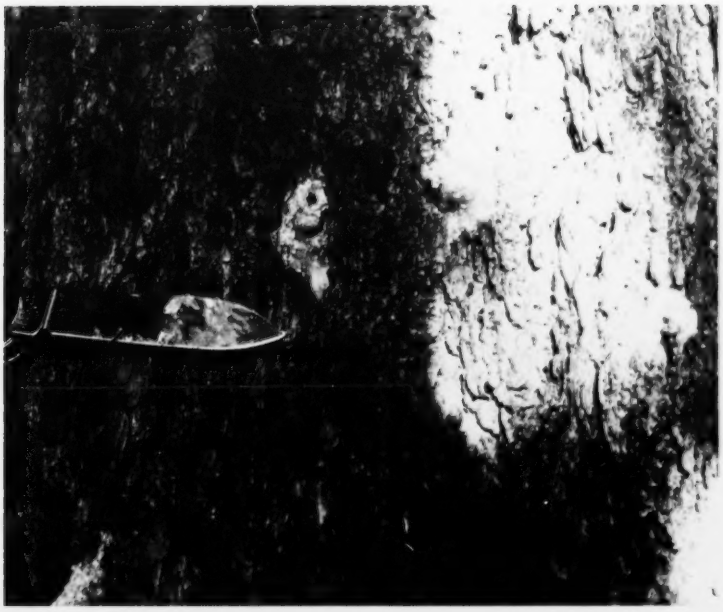

Figure 1. Pitch tubes indicative of the tree's resinous response to beetle infestation. (Photo courtesy of L. Allen, Paprican).

## 1.2 Extractives content of sound lodgepole pine

Prior to discussing the mountain pine beetle attack-induced changes of extractives, a short overview of extractives content and composition in sound lodgepole pine is warranted. Sound lodgepole pine extractives have been studied by various researchers [23-35]; however a comparison of the results is difficult as different techniques for extraction (acetone, ether, alcohol-benzene extraction) have been used and also different parts of the trees have been studied (sapwood, heartwood, mature or juvenile wood, whole stems). Table I gives an overview of the different numbers for extractive content of sound lodgepole pine that can be found in the literature.

**Table I.** A compilation of extractive contents found in sound lodgepole pine by various researchers.

| Author | Alcohol-benzene sol. % | | | Ether sol. % | | | Acetone sol. % | | |
|---|---|---|---|---|---|---|---|---|---|
| | Whole | Juv. | Mat. | Whole | Sap | Heart | Whole | Sap | Heart |
| Woo *et al.* 2005 [23] | | | | | | | | 1.8-2.2 | 2-4 |
| Gao *et al.* 1995 [24] | | | | | | | | 1.9-2.3 | 9.7-12.4 |
| Hatton & Hunt 1991 [25] | | 3.6-9.2 | 2.7-5.1 | | | | | | |
| Kim 1988 [26] | 2.94-3.85* | | | | | | | | |
| Isenberg 1980 [27] | 3.5 | | | | | | | | |
| Lieu *et al.* 1979 [28] | | | | | 0.31 | 0.91 | | | |
| Fengel 1975 [29] | | | | 2.3 | | | | | |
| Shrimpton 1973 [30] | | | | | | | | 2.7-7.0+ | 3.6-6.5+ |
| Shrimpton 1972 [31] | | | | | | | | 2.7 | 5.6 |
| Rogers *et al.* 1969 [32] | | | | | | | 4.93 | | |
| Anderson *et al.* 1969 [34] | | | | | 3.9 | 3.6 | | | |
| Kurth 1950 [35] | | | | 1.56 | | | | | |

* Extraction by ethanol-toluene. Variation is for trees from different latitudes (40-60°).

+ These numbers show variations between individual trees.

Most data have been gathered for acetone extractives. In general, the extractives content of sapwood is lower than that of heartwood, however variations between individual trees can be large [30]. In general, the sapwood extractives content is in the range of 2% to 3%. The extractives content for heartwood varies between 2% to 12.5%. Gao et al. [24] report values between 9.7% to 12.4% which seem high. Typical heartwood extractives contents for sound lodgepole pine from 1.5% to 6% are more common.

The distribution of acetone extractives between different lipid classes found by various researchers are given in Table II. The large variations found in lipid class distribution by different researchers are probably due to the large variability between individual trees (see Shrimpton [30], who shows extractive variations for five different trees). Overall, free acid content seems to be lower in the sapwood than in the heartwood. Shrimpton [30] found that in sapwood, the resin acid content exceeds that of fatty acids in the free acid fraction. This holds for heartwood, but differences are much less pronounced. For whole wood samples, Rogers *et al.* [33] also found resin acids dominant. The relative amount of neutrals in the extractives vary more widely than for free acids. Gao *et al.* [24] observed a significant difference between sapwood and heartwood regarding the neutral and free acids content. The sapwood had more neutrals, while the heartwood contained much more free acids. Shrimpton [30] did not find such a pronounced difference in neutrals and free acids concentration for sap- and heartwood. In the neutral fraction, Gao *et al.* [24] found glycerides, steryl esters and waxes to dominate, which was also noted by Shrimpton [30]. These components are saponifiable, which would result in higher fatty acid contents during kraft pulping. In contrast, Woo *et al.* [23] found sterols to be the main fraction of the neutrals.

**Table II.** Acetone extractives of sound lodgepole pine by different classes. Numbers for classes are given in % of OD wood, and in relative proportion (%) of overall acetone extractives (in brackets).

| | Woo *et al.* [23] | Gao *et al.* [24][1] | | Shrimpton [30][2] | | Rogers *et al.* [33] |
|---|---|---|---|---|---|---|
| | Sap | Sap | Heart | Sap | Heart | Whole |
| **Free acids** | 0.35 (18.0) | 0.35-0.42 (18.5-19.3) | 5.4-6.7 (54.1-55.5) | 2.0-2.1 (30.0-74.1) | 2.3-3.5 (36.9-63.9) | 1.45 (61.0) |
| Fatty acids | | | | 0.25-0.48 (5.0-17.0) | 0.84-1.57 (17.8-32.0) | 0.33 (11.4) |
| Resin acids | | | | 1.53-1.80 (23.0-58.1) | 1.16-1.93 (17.8-39.4) | 1.15 (39.6) |
| **Neutrals** | 1.6 (82.0) | | | 0.6-2.6 (21.4-67.1) | 1.2-3.9 (24.5-60.0) | 1.42 (49.0) |
| Triglycerides | 0.2 (10.3) | 1.1-1.3 (58.3-58.5) | 0.58-0.73 (5.9-6.0) | | | |
| Sterols | 1.0 (51.3) | 0.02-0.03 (1.2) | 0.08-0.10 (0.8) | | | |
| Steryl esters/waxes | 0.4 (20.4) | 0.15-0.21 (8.0-9.8) | 0.25-0.33 (2.1-3.4) | | | |
| Monoglycerides | | 0.01-0.02 (0.7-1.2) | 0.39-0.53 (3.2-5.5) | | | |
| Others | | 0.23-0.25 (10.5-12.9) | 2.8-4.2 (28.5-34.0) | | | |

[1]Variation given is between inner and outer sapwood/heartwood. [2]Variation given is between five sample trees.

Within the fatty acid fraction, linoleic and oleic acids are main components in both sapwood and heartwood [23,30,33]. Gao *et al.* [24] also found significant amounts of linolenic and palmitic (the latter in sapwood only), but this was not the case in other studies. Of the free resin acids, isopimaric, abietic, dehydroabietic and to a certain extent neoabietic are the main ones, but relative fractions differ for sapwood and heartwood. Gao *et al.* [24] found palustric to be the most important free resin acid in both sap and heartwood, but this is not evident in other studies.

The main fatty acids recovered through saponification of the neutral fraction are oleic and linoleic acids which are found in both sapwood and heartwood [23,30, 33]. Gao *et al.* [24] noted that a large part of the bound acids in heartwood were not identified in their study. According to Shrimpton [30], the relative distribution of acids is quite similar for the free acids and saponifiables. He also noted that most of the neutral fraction consisted of glycerides and waxes which are saponified. Both observations were shared by Rogers *et al.* [33]. The major components of the non-saponifiables were glycerol, with α-terpineol and β-sitosterol also recovered [30]. The most common monoterpene in both sapwood and heartwood is β-phellandrene [31,34], but $\Delta^3$-carene, β-pinene, limonene and α-phellandrene were also found in higher amounts.

In general, it was noted that the extractives in heartwood decrease with stem height, while the extractives of sapwood increase or remain constant [23,26]. Kim [26] also noted a positive correlation of extractives in lodgepole pine with latitude and elevation, as well as with tree diameter, which can be attributed to differing amounts of heartwood for these variables.

## 1.3 Changes of extractives content in lodgepole pine related to mountain pine beetle attack

Individual lodgepole pine trees respond differently to mountain pine beetle attack. In endemic situations, a fast and intense secondary response to beetle attack seems to be the determining factor whether a tree can withstand or will succumb to attack. In most studies the response is described as rather general [21,22], and thus a quantitative response seems to be more important than a qualitative response.

However, during an epidemic, when trees come under mass attack, even an extensive secondary resinosis cannot fend off attack and only a few trees within a stand may survive [6]. The intensity of the secondary response is likely influenced by the amount of wounding [22] and decreases with increasing attack. The survival of a tree during epidemics thus supposedly depends not only on the extent of secondary resinosis, but also on the resin composition, which is likely related to genetic factors [36]. The differences regarding extractives in the response of a susceptible or resistant tree (respectively the differences between resinous and non-resinous response) are the subject of many studies [17,21,22,30,36].

The secondary resinosis will cause changes in overall extractive content and composition, as resin is synthesized in the parenchyma cells. The primary response is merely a redistribution of existing oleoresin to the wound site. The changes from secondary resinosis can be seen starting shortly after the initial attack on the tree, and changes will occur until the tree dies. Any further changes in extractives content and composition after that are due to utilization of compounds by the fungi, or to abiotic induced changes. The synthesis of extractives in response to mountain pine beetle attack directly has been the subject of only few studies [23, 30], but more can be found on the response of trees to inoculation with fungi that are associated with the mountain pine beetle [20-22,37,38]. In evaluating these studies, care needs to be taken not only as to whether they refer to the whole tree or only wound tissue, but also to the time period between sample taking and tree death (or initial attack on trees). Many studies focus solely on changes of monoterpene content in trees under attack, as monoterpenes were commonly assumed to be the most important compound in the resistance of conifers to bark beetle attack [36,38]; however some studies that include a wider spectrum of extractives are available.

Raffa and Berryman [21], in a study of physiological differences between lodgepole pines that are resistant or susceptible to mountain pine beetle attack, looked at the monoterpene content of reaction tissue after inoculation with *Europhium clavigerum* as one factor that could determine resistance. They did not find any significant qualitative differences in the monoterpene composition of constitutive and reaction tissue within one tree, or between resistant and susceptible trees. However, the α-pinene and limonene contents increased in the wound tissue compared to constitutive phloem (for both resistant and susceptible trees), while Δ-3-carene and sabinene decreased. However only α-pinene and Δ-3-carene are major constituents (each is 3% to 4% of overall monoterpenes), and even these are minor compared to the high amount of β-phellandrene (75%-80%). The main difference between resistant and susceptible trees that was

observed is that the former had higher amounts of monoterpenes than the latter. In summary, they found the response to be a rather generalized response that was more quantitative than qualitative.

Changes in extractives in the wound tissue of trees attacked by mountain pine beetle were also studied by Shrimpton [30] who sampled wound response tissue from trees that successfully resisted beetle infestation over time (5 weeks, 1 year, 2 years after attack, resinous response). He compared these trees to the wound response tissue from trees that succumbed to infestation (5 weeks after initial attack, non-resinous response), and to sound sapwood and heartwood for comparison. Extractives studied were the steam volatiles, and the acetone- and methanol-soluble fractions. He noted higher levels of monoterpenes for the resinous response, which over time receded (presumably due to losses to the atmosphere in open wounds, polymerization, or further metabolism of monoterpenes in parenchyma cells). The large increase in monoterpenes levels, without a concurrent increase in resin acid levels, suggests that the wound response is indeed the synthesis of certain extractives and not merely an increased flow of oleoresin to the wound. It appears that the production of monoterpenes is a specific response to wounding by lodgepole pine species as a result of slow death of parenchyma cells. Other results of wounding that were observed are a slight decrease in fatty acids, and an increase in resin acids and neutrals. Sugars also decreased noticeably. Free acids, neutrals and phenolics in the resinous response increased to final concentrations about the same as found in heartwood, but at a much slower rate than monoterpenes. For the non-resinous response, a small increase in monoterpenes and resin acids as a result of oleoresin flow into the area is observed, but utilization of cellular contents by the fungi prevents increased amounts of extractives being formed otherwise. Sugars decrease noticeably, presumably due to utilization by fungi.

In the steam-volatile fraction, the main difference found between unattacked and attacked trees was in the relative amount of β-phellandrene. β-phellandrene was the predominant monoterpene in the resinous response (51% after 5 weeks decreasing to 35.4% after 2 years), but was low in the non-resinous response (10.1%) and intermediate in unattacked sapwood (25.6%). The non-resinous response showed a marked increase in 3-carene (30.6% compared to 15.2% in unattacked sapwood).

For acetone extraction, main differences in free fatty acid composition are for linoleic acid (a fatty acid) which decreased in the resinous and non-resinous response (as a fraction of overall acids; as a fraction within the fatty acids not much change was observed), abietic and pimaric acid (resin acids) which increased in both the non-resinous and resinous response and dehydroabietic acid which increased only in the non-resinous response. The free acids that were found were the same in all samples, except lauric acid which was found only in the non-resinous response and the resinous response after five weeks, but not in unattacked sapwood or heartwood.

Of the fatty acids obtained after saponification of the neutrals fraction, main differences between unattacked and attacked wood were in oleic acid which had increased in the non-resinous response, linoleic which was lower in both the resinous and non-resinous

response, and palmitic which had increased in both resinous and non-resinous response. The distribution of free acids and acids obtained after saponification is shown in Table III and Table IV.

**Table III.** Free acids of unattacked sapwood and heartwood, and wound response of lodgepole pine attacked by the mountain pine beetle (Shrimpton [30]).

| | Wound response tissues | | | Unattacked sapwood | Unattacked heartwood |
|---|---|---|---|---|---|
| | | Resinous | | | |
| | Non-resinous | 5-week | 2-year | | |
| Lauric | 0.6* | 0.5 | - | - | - |
| Myristic | tr | - | - | - | - |
| Unidentified | tr | - | - | - | - |
| Palmitic | 4.2 | 0.8 | 0.7 | 1.6 | 1.8 |
| Palmitoleic | 0.5 | Tr | - | 0.7 | 0.8 |
| Stearic | tr | Tr | - | - | - |
| Oleic | 9.4 | 4.5 | 7.5 | 5.9 | 10.4 |
| Linoleic | 4.0 | 4.0 | 6.0 | 10.5 | 18.2 |
| 5,9,12-octadecatrienoic | tr | - | - | 0.5 | tr |
| Arachidic | 1.0 | 0.5 | 0.5 | 1.1 | 1.5 |
| Linolenic | tr | - | - | 0.5 | tr |
| Unidentified | - | - | tr | tr | tr |
| Behenic | tr | 0.5 | 0.8 | 2.6 | 3.6 |
| Pimaric | 5.9 | 9.2 | 6.1 | 3.8 | 4.4 |
| Sandracopimaric | 1.0 | 2.3 | 2.0 | 2.6 | 1.1 |
| Levopimaric/palustric | 1.7 | 0.5 | 9.5 | 8.8 | 4.5 |
| Isopimaric | 11.8 | 15.2 | 6.9 | 10.3 | 8.4 |
| Abietic | 27.1 | 32.9 | 31.4 | 19.5 | 14.6 |
| Dehydroabietic | 30.3 | 23.8 | 23.5 | 24.7 | 25.8 |
| Neoabietic | 2.1 | 4.7 | 5.9 | 6.3 | 4.8 |

*Values are percentage of fraction
Note: tr = trace quantities less than 0.5%

**Table IV.** Acids obtained after saponification of neutrals of unattacked sapwood and heartwood and wound response of lodgepole pine attacked by the mountain pine beetle (from Shrimpton [30]).

| | Wound response tissues | | | Unattacked sapwood | Unattacked heartwood |
|---|---|---|---|---|---|
| | | Resinous | | | |
| | Non-resinous | 5-week | 2-year | | |
| Lauric | 1.8* | - | 0.8 | - | - |
| Myristic | 0.5 | 1.1 | 7.8 | 1.5 | 2.0 |
| Unidentified | 0.5 | - | - | - | - |
| Palmitic | 13.0 | 17.0 | 15.1 | 8.0 | 9.1 |
| Palmitoleic | 7.6 | 4.8 | 3.4 | 1.8 | 2.3 |
| Stearic | 3.3 | 1.2 | 0.8 | tr | tr |
| Oleic | 42.3 | 33.3 | 27.4 | 30.0 | 25.6 |
| Linoleic | 23.0 | 23.1 | 19.6 | 47.8 | 54.2 |
| 5,9,12-octadecatrienoic | tr | - | tr | tr | tr |
| Arachidic | 5.8 | 7.7 | 14.7 | 7.1 | 4.3 |
| Linolenic | tr | 0.8 | 0.5 | 1.2 | 0.5 |
| Unidentified | tr | 2.9 | 1.3 | 1.0 | 1.6 |
| Behenic | 2.9 | 7.4 | 8.2 | 1.5 | tr |

*Values are percentage of fraction
Note: tr = trace quantities less than 0.5%

The four phenolics of lodgepole pine heartwood: pinosylvin, pinosylvin monomethyl-ether, pinobanksin and pinocembrin [39], were found in the non-resinous as well as in the resinous wound response tissue, but not in unattacked sapwood.

The numbers for terpenes in wound tissue of the resinous response compare relatively well to numbers found in an earlier study [37]. They observed the response of lodgepole pine seedlings to inoculation with *Europhium clavigerum* and compared it to the response of mature pines. After 60 days from inoculation, they sampled the resinous tissues from seedlings and also from four resistant mature pine responses. In the resin-soaked sapwood from inoculated seedlings, they found β-phellandrene as the main component, and 3-carene, β-pinene, camphene and α-pinene as secondary components, and trace amounts of myrcene, limonene and p-cymene. The response from mature trees showed the same compounds and was also comparable in distribution of these compounds. They also found the four phenolics of lodgepole pine heartwood to be present in the resinous response of seedlings as well as mature trees.

Following their earlier work, Raffa and Berryman in 1983 [22] again studied the response of lodgepole pine to inoculation with *Europhium clavigerum*. They determined the acetone-soluble fraction of phloem tissue samples of 78 lodgepole pines prior to and following artificial inoculation. In order to attribute changes in host chemistry solely to those occurring locally within the phloem (as opposed to the phloem-resin reaction zone samples in their earlier study [21]), they excluded the liquid resin flow at the wound site during sampling. A qualitative analysis of each chromatogram of acetone extracts showed that they can be divided into four regions, the first one composed of monoterpenes, the second one of oxygenated monoterpenes, unidentified alcohols and methyl alcohol, the third one sesquiterpenes, bornyl acetate and some uncharacterized complex structures, and the fourth one is comprised of a heterogeneous group of unknown, less volatile and highly complex entities. After 3 and 7 days following inoculation, they noticed an overall increase in the acetone extractives of 3 and 4.5 times respectively, over the constitutive value. Relative proportion of the different groups of extractives also changed, with a net increase in all groups, but a relative decline of groups 1 and 2 of overall extractives while the proportion of group 3 and 4 increased (Table V). They also observed qualitative changes with the appearance of compounds that are not found in the acetone extractives of constitutive phloem. Qualitative changes occurred in all groups except group 1, and some of the most abundant compounds were compounds not observed in uninjured phloem. As in their earlier study, they described the response to inoculation as a very generalized response.

**Table V.** Relative composition (in %) of acetone-soluble extractives in lodgepole pine phloem following fungal inoculation (Raffa and Berryman [21])

| | Days after inoculation | | |
|---|---|---|---|
| Chromatogram section | 0 | 3 | 7 |
| 1 (monoterpenes) | 56.2 | 52.2 | 32.3 |
| 2 (oxy-monoterpenes, alcohols) | 12.3 | 6.7 | 8.2 |
| 3 (sesquiterpenoids) | 6.9 | 7.6 | 20.1 |
| 4 (heterogeneous) | 24.6 | 33.5 | 39.4 |

They then looked at differences between trees that were susceptible or resistant to beetle attack and found no significant quantitative or qualitative differences between the uninjured phloem. In the response to fungal infection, surviving trees, however, showed a higher total accumulation of acetone extractives after 7 days. They note that resistant trees respond with a more rapid and pronounced accumulation of acetone extractives and this difference can be found mainly in groups 3 and 4, which are the more complex non-volatile substances that have not received much attention in earlier studies.

A last issue they looked at was simulation of mass attack through applying multiple inoculations. They found a diminished average accumulation of monoterpenes per inoculation for high inoculation densities. Even the total monoterpene accumulation in a tree section reached a maximum at a certain number of inoculations and diminished thereafter. Unfortunately, they do not report levels of other extractives than monoterpenes as a function of inoculation density.

Further evidence that during secondary resinosis some extractives are synthesized that usually do not occur in lodgepole pine was given by Ayer and Migaj [40]. They used benzene extraction in an attempt to isolate compounds that are suspected to cause the blue-stain from diseased lodgepole pine. They could not find any of these suspected compounds, but some resin acids that they isolated some are found which have not previously been reported for lodgepole pine. They conclude that these acids may be formed by fungal-induced enzymatic oxidation of dehydroabietic acid commonly present in the tree. Some fungi are known to oxidize resin acids and generate these types of compounds [41]. The compounds in question are 15-hydroxydehydroabietic acid, 7β-hydroxydehydroabietic acid, 7α-hydroxy-dehydroabietic acid and 7-oxodehydroabietic acid. Spectra for these compounds are given in some detail.

Another study that mainly focuses on the monoterpene and diterpene synthesis of oleoresinosis, but also mentions other extractives found in wound tissue, was conducted by Croteau *et al.* [38]. They focused on the monoterpene and diterpene biosynthesis in lodgepole pine saplings that are infected with the blue-stain fungus *Ceratocystis clavigera*. They used gas chromatography to recover about 85% of the monoterpenes and 80% of resin acids (in form of methyl dehydroabietate) from the wound tissues and control tissues of uninfected trees. After a 10 day period, they found significant increases of the monoterpene olefins α-pinene, β-pinene, 3-carene and β-phellandrene. Levels of α-phellandrene and limonene decreased, possibly due to volatility losses. They confirmed the presence of abietic-type resin acids as would be expected from studies on mature trees. A corresponding increase in activity of the relevant terpene cyclases was also determined. The non-volatile neutral components increased about 2.5-fold and showed a very complex mixture of more than 20 components.

The most recent study looking at the influence of mountain pine beetle attack on wood morphology and chemistry is by Woo *et al.* [23]. This work contains some preliminary experimental work regarding the influence of mountain pine beetle attack on extractives. To our knowledge, this is so far the only study that looks at changes in extractives caused

by mountain pine beetle attack for the whole stem, and not only wound tissue. A dead (infestation was estimated to have occurred 8 month prior to harvest) and a sound lodgepole pine tree of same size from the same site were harvested and extractives were determined by acetone extraction. Total extractives were found to be in the range of 2% to 4% for the sound heartwood, and in about the same range for infested heartwood. The total extractives of sound sapwood were lower than of heartwood at about 1% to 2%. For sapwood the infested wood, however, shows even lower extractive content than the sound sapwood (about 0.8% points lower). Heartwood extractives decrease with tree height (sound and infested wood), while sapwood extractives increase (again for both sound and infested wood). These findings should, however, be taken with caution, as they are based on only one sample tree. Between-tree variation of extractives can be high [31] and thus a generalization of the findings of Woo *et al.* is difficult.

Woo *et al.* also found not only total content, but also relative content of different extractive components in sapwood to change with infestation. Infested wood shows a higher proportion of fatty and resin acids (these were grouped together), but lower proportion of sterols (most noticeable), steryl esters and triglycerides, likely an effect of wood extractive utilization by fungi that continues after the tree dies. This hypothesis is supported by studies of the removal of toxicity from pulp mill effluents with the use of certain blue-stain fungi [42]. It was shown that many fungi, among them blue-stain fungi, are effective at reducing overall resin content in wood [41], however most of them at the same time fail to remove toxicity. As the toxic components of the effluents are mainly resin and long chain fatty acids, the findings imply that most blue-stain fungi will utilize sterols, steryl esters, triglycerides, diglycerides and shorter chain fatty acids, but not longer chain fatty acids and resin acids. In standing wood infected by blue-stain fungi, a change in composition of wood extractives over time after tree death thus could be expected.

Some general numbers of extractive content in mountain pine beetle infested lodgepole pine are reported in Trent et al. [4] and Dalpke et al. [43]. In Trent et al. [4], the acetone extractive amount of lodgepole pine from different sites in British Columbia is reported. Trees have been dead for 2 to 15 years. Extractives are between 1.5% and 6% of oven-dry wood, with the majority between 1.5% and 4.5%. This lies in the same range as found for sound lodgepole pine (Table I). No dependence of extractives on time-since-death is apparent. However, no recently killed trees or green pine trees, and only a few trees that have been dead for longer than 5 years, were sampled. In Dalpke et al. [43], extractives for red stage lodgepole pine trees are reported. Kill date was not conclusively determined, but is probably around 2 years. Samples are also from different sites in BC, but overall the sample size is smaller than in Trent et al. [4]. Reported lodgepole pine extractives are in the range of 3% to 5.5% and thus at the higher end of the ranges found for sound lodgepole pine.

## 1.4 The impact of extractives and other factors on foaming problems and tall oil production in the pulp and paper industry

### *1.4.1 A short review of the principles of foaming*

Films formed by adjacent bubbles in a pure, low-viscosity liquid are extremely unstable, and thus a pure liquid will not form foams. Adding a surfactant will lower the surface tension at the gas-liquid interface, making the formation of foam easier. Also, many surfactants help stabilize the foam. Good reviews of foam formation and stability are given in Keegan et al.[44-47]. A brief summary is given below.

The aqueous foams formed in a low-viscosity liquid containing a third component are thermodynamically unstable and subject to foam destruction by two major effects: drainage and bubble rupture. In foam drainage, a freshly formed foam with high water content and small, spherical bubbles is subject to gravitational forces. Liquid will drain out of the foam, the gas fraction increases and the bubbles are distorted into polyhedra. Due to differences in capillary pressure, gas diffuses from smaller to larger bubbles, and the films at the top of the foam thin and are more susceptible to collapse by mechanical shock or vibration [47]. Foam drainage, as a foam destroying process, is time dependent and thus only important in applications where sufficient time for drainage is given. For example, in the case of foaming during brownstock washing, available time for foam to break down is short and thus foam drainage is likely an unimportant process.

The second mechanism, bubble rupture, is the most important mechanism for destroying foam. Bubble rupture occurs when small holes form in the liquid film as a result of disturbances in the foam lamella. Rupture of surface bubbles will decrease the foam volume, while rupture of bubbles within the foam will lead to larger bubbles thus decreasing the area of liquid/gas interface.

Foams can be stabilized by different mechanisms, leading to long-lived foams that can be problematic in pulp and paper processes. The adsorption of surfactant molecules at the gas-liquid interface can lead to a high viscosity at the interface different from the bulk viscosity of the liquid, possibly with non-Newtonian behaviour. Such a visco-elastic film opposes mechanical fluctuations, thus preventing the formation of holes in the film. Also, for a very viscous interface, the liquid drains more slowly out of the foam. A second stabilizing effect is the so-called Marangoni effect. If a new surface area is formed in the foam, or the existing foam film is stretched locally, the concentration of surfactant molecules in these areas will be lower, as surfactants are large molecules that need time to diffuse. The surface tension, thus, will be higher and the gradient in surface tension works as a restoring force against the formation of new surfaces.

Steric stabilization occurs if water-borne polymers are absorbed at the interface that would rather not mix with each other. In that case, once the film drains, the polymers on opposing surfaces will repel each other and resist further drainage, much like an osmotic pressure.

In the same way as steric stabilization, opposing electrical layers lead to a repulsive force when overlapping, thus resisting further drainage. However, if electrolyte concentration in a liquid is high, this mechanism probably does not play a significant role.

As a fifth stabilizing mechanism, a concentration gradient at the foam surface will result in an osmotic pressure, which will cause material to flow, thus leveling out the concentration and healing the disturbance in the lamella, similar to the Marangoni effect.

In practice, foaming liquids are described using two properties, their tendency to foam (foaminess) and their foam stability, measured as the time they last. However, measurements of foaminess and foam stability are not standardized. Many different methods to measure these variables exist, and most measurements depend on the measurement method and settings, making it difficult to compare results. A relatively simple and general method to describe foaminess is based on the so-called Bikerman formula [48]. When bubbling a gas through a liquid, the volume of foam observed under equilibrium conditions is proportional to the gas flow rate. The proportionality constant depends on the liquid and is termed the foaminess or sigma value. It is based on the measurement of foam volume produced, aeration time and gas volume introduced:

$$\Sigma = \frac{v_0 t}{V}$$

where

$\Sigma$ = foaminess [s]
$v_0$ = foam volume in [ml]
$t$ = time in [s]
$V$ = total gas volume in [ml]

Foaminess $\Sigma$ has the dimension of time and represents the time an average bubble exists in the foam before bursting. While the measurement of $\Sigma$ is relatively simple, care needs to be taken to reach equilibrium conditions. The method is most suited to foams of intermediate lifetimes. See Bikerman [48] for a more detailed discussion of the determination of foaminess.

### *1.4.2 Factors affecting foaming with a special focus on extractives*

In kraft pulping, foaming problems arise mainly during brown stock washing, but are also found in secondary effluent treatment systems [49]. Foaming problems in the pulping and bleaching stages of a kraft mill are less common. During brown stock washing, foaming decreases efficiency as filtration resistance and washing losses increase [49,50]. Washing losses carried over into oxygen stages of the bleach plant will decrease the efficiency of bleaching chemicals resulting in less kappa reduction and also reduced pulp strength [51]. The black liquor in kraft pulping is an excellent foaming liquid, as it contains ample amounts of surface active substances. Such substances, which have a hydrophilic part as well as a hydrophobic part, are very common foaming agents [52] and foam stabilizers. The sources for surface active substances are wood extractives as well as derivatives of

lignin; however the following discussion will focus mostly on the extractives related substances. Also, foaming problems are not limited to kraft pulping operations. Large amounts of wood resin components can be present in mechanical pulping operations where they cause similar problems with foaming, mostly during the papermaking process and in secondary effluent treatment.

In black liquor, extractives related surfactants generally are found in the form of dissolved black liquor soap [48], with molecules that have carboxylate groups as the hydrophilic part and hydrocarbons as the hydrophobic part. The hydrocarbons can be saturated or unsaturated chains from fatty acid soaps, or cyclic hydrocarbons from resin acid soaps and sterols [53]. Stephenson [54] notes that the foaming tendency of black liquor is more pronounced in sulphate mills than in soda mills, and greater for processes that use the more resinous woods like the southern pines. This implies that most likely the amount of resin soap in black liquor plays an important part in governing the foaming propensity of black liquor, although the composition of resinous substances can also be a factor. In the same context, foaming tendency of green chips is greater than for seasoned chips. Green chips have a greater extractives content and also different composition of extractives compared to seasoned chips. Lastly, it is observed that the foaming tendency of black liquor is greatest for small concentrations, while at larger concentrations of more than 35% solids, the foaming tendency decreases markedly. The positive correlation between the amount of extractives in the raw material (wood species) and amount of produced foam was also noted in Waldichuk [55]. Higher amount of extractives (as for interior species compared to coastal species) and thus higher concentration of surface-active substances, were also linked to increased foam-stability [56], but no further analysis of extractives was done, thus the increased foam stability could also be caused by a different composition of extractives or differences in the concentration and composition of other surface-active substances.

While the importance of total wood resin regarding foaming tendency is undisputed, little is known about the contribution of specific components of wood resin to foaming tendency and stability. A study by Tay [57], even though unrelated to foaming issues, confirmed the differences in influence on surface tension for fatty and resin acids. He added different amounts of fatty acids (a mix of 50% oleic and 50% linoleic), resin acid (abietic) or the float extractive from a high-yield sulfite weak liquor (which contains a mix of fatty and resin acids) to water and showed that the drop in surface tension was greatest for the fatty acids, followed by the float extractive. He also looked into the influence of lignosulfonates on surface tension, which was only small. There were some uncertainties in the surface tension measurements, as results from two different measurement methods showed poor correlation. While lignosulfonates are not the topic of this review, it should be noted here that some authors consider the influence of dissolved lignin and its derivatives on foaming propensity to be more important than the influence of extractives [58,59]. Guo and Coller [60] also measured surface tension and found that the surface tension decreases for liquids with high concentrations of lignosulfonates. A study of spent sulfite liquor found lignosulfonates as well as fatty acids and resin acids to be important foaming agents [61]. These observations show the importance of considering all potentially surface-active substances if a thorough

investigation into foaming propensity of liquids throughout pulp and paper operations is done, including extractives, lignin-related substances as well as any other possibly surface-active substances.

While Green *et al.* [58] showed that for sawdust from ground jack pine, foaminess was mainly caused by lignin-derived substances, he also observed the foam to be stabilized by pitch in the liquid. The importance of lignin and extractives are also compared in Carpenter and Gellman [62] for selected data from biologically treated and raw mill effluents. They concluded that the foaminess of a liquid is related to biologically stable materials, like lignin and its derivatives, while the foam stability is influenced by the more readily degradable materials such as the soaps from extractives. A further indication for the foam-stability enhancing abilities of extractives was found by Dorris *et al.* [63]. In this study of deinking, a tall oil mixture used as flotation collector in a deinking procedure was found to produce more stable foams than the commonly used saturated fatty acids. The tall oil mixture was rich in resin acids and thus results indicated that resin acids or a mixture of resin and fatty acids might produce more stable and thus detrimental foams. It remains unknown if the same would be true under conditions found in kraft pulping or waste water treatment. However, Laxén [50] also points towards the ratio of fatty soap to resin soap as one factor in foam stability, but without further elaborating. Kleinert and Ruck-Floriantschitsch [59] found the addition of rosin size to sulfite spent liquor had little influence on foaminess or foam stability, but no further specification of the added rosin size is given. The addition takes place in an acidic environment, which is again different from conditions of black liquor from kraft pulping.

The influence of total extractives content, composition of extractives, and ratio of fatty soap to resin soap on foaminess and foam stability is closely interrelated with other factors, such as temperature, pH, sodium concentration, soap concentration, suspended fine material and liquor viscosity. Some of these factors obviously will influence the ratio of solid soap to soap in solution, with the latter being a main cause for foaming.

The pH of a solution is an important factor in foaming and foam stability in that it affects the surface tension. For spent sulphite liquor, it was found that the surface tension was lowest around a neutral pH, somewhat higher in the acidic range, but highest for alkaline pH values around pH 10 [62,64]. In line with this finding, the equilibrium foam volume during foaming experiments was also observed to be 80% higher at high alkaline pH values than at low acidic pH values. This was attributed to resin and fatty acids ionizing by losing a proton at a high pH, thus becoming more surface active [65]. Kleinert and Ruck-Floriantschitsch [59] also found the pH to influence foaming and foam stability in spent sulphite liquor. They found increased foaming tendency at higher pH values only; however foam stability was greatly enhanced with increasing acidity and alkalinity, with a minimum around the neutral point. Besides pH, the foaming effect of surfactants also depends on temperature [66].

Sodium and soap concentrations and solubility are also important factors for foaming issues. Indirectly, a high sodium and soap concentration in initial washing stages can lead to insufficient washing, as some of the soap might be in the solid state [50,67]. The

increased soap concentration in later stages then can lead to foaming problems. Efficient removal of wood resin can be achieved by maintaining a low critical soap micelle concentration (and thus high solubility of soap) and a high stable salt concentration [67]. The critical soap micelle concentration is related to the soap composition, which should be between 1:1 and 2:1 for the fatty acid/resin acid soap ratio [52]. Not surprisingly, insufficient washing thus often can be traced to large variations in extractives content [68]. Foam stability also was observed to depend on sodium and soap concentration [50]. Sodium and soap concentration, resin to fatty acid ratio, pH, temperature, washing efficiency and foaming tendency and stability are all closely interrelated and, thus, need to be considered when tracing foaming problems in kraft pulping operations.

Suspended particulate matter is reported to enhance foam stability in paper machine effluent in Kleinert and Ruck-Floriantschitsch, Surewicz and Modrzejewski, and Dalpke et al. [59,64,69]. Kleinert and Ruck-Floriantschitsch [59] found the foaming tendency as well as foam stability of sulphite spent liquor to depend also on the amount of fibres in the liquor. Guo and Coller [60], however, did not find a difference in foam stability for filtered or unfiltered samples of a paper mill wastewater stream.

While this discussion offers some possible explanations of how the use of mountain pine beetle-infested wood and increased foaming tendency might relate, too little is known about the actual changes in wood extractives caused by mountain pine beetle attack and about the influence of specific extractives components on foaming to make any definite statements. More work is needed, particularly work that investigates the foaming tendency of process streams originating from the pulping of beetle-killed wood, and at the same time determines extractives (and other surface active components) contained in such streams.

# 2 Material and Methods

## 2.1 Wood Sources

Different wood samples were used in this study. These included:

Ninety-seven cores (12 mm diameter) taken from different lodgepole pines grown in two different biogeoclimatic ecosystem (BEC) classification zones, the sub-boreal spruce (SBS) and sub-boreal pine spruce (SBPS). The trees were harvested from different sub zones within these BEC zones. Their source and characteristics are summarized in Table VI and discussed in detail in MPBI Project 8.65 [69].

Of the 97 samples, nine were selected for chipping and pulping as outlined in section 3.3 and Table IV of Dalpke et al. [69]. These included three green stage, two red stage and four grey stage chip samples. In this study, "green stage" wood refers to lodgepole pines that have been unattacked by mountain pine beetle. The TMP pressates and weak black liquors produced in MPBI Project 8.65 [69] were used in this study to investigate their foaming propensity.

Chip samples were obtained from seven interior BC pulp mills that pulped mountain pine beetle-killed lodgepole pine.

Table VI. Summary of 97 cores from Dalpke et al. [69].MPB = mountain pine beetle

| BEC | Subzone | Site index | MPB Stage | Time-Since-Death (TSD) | number of cores |
|---|---|---|---|---|---|
| SBS | Mc2 | 18 | green | 0 yr | 18 |
| SBS | Wk3 | 18 | green | 0 yr | 18 |
| SBS | Mc2 | 18 | grey | 4 yr | 14 |
| SBS | Vk1 | 15 | red | 2 yr | 2 |
| SBS | Mc2 | 18 | grey | 8 yr | 5 |
| SBPS | xc | 15 | green | 0 yr | 7 |
| SBPS | xc | 15 | red | 2 yr | 27 |
| SBPS | dc | 15 | grey | 4 yr | 3 |
| SBPS | xc | 15 | grey | 15 yr | 3 |

## 2.2 Acetone Extracts

Wood samples (cores or chips) were air-dried and the moisture content determined (oven-dried overnight at temperature of 105 ±3°C). Wood samples (~5 grams) were extracted with acetone for 4 hrs using a Soxhlet apparatus. The extracted cores or chips were collected and air-dried overnight. Extractives, in acetone, for each sample were reduced in volume via rotary evaporation and by warming over a stream of $N_2$. When reduced to an approximate volume of 1 ml, the sample was quantitatively transferred to a tared glass test tube and freeze-dried. Total extractives were determined gravimetrically and expressed as a percentage of the dry weight of wood extracted.

## 2.3 Pulping

All chips were kraft pulped to a target kappa number of approximately 30 as described in section 2.3.3 of [69]. Chip samples were also thermomechanically pulped as detailed in section 2.3.4 of [69]. Kraft weak black liquors and TMP pressates were collected and used in subsequent experiments.

## 2.4 Characterization of weak black liquor samples and TMP pressates

The characterization of black liquor samples included tests for viscosity, solids content, REA, and specific gravity. Viscosity measurements were made using a modified LVII+ viscometer equipped with a UL adapter with a copper heating/cooling coil connected to a bath. The UL adapter (Ultra Low) was necessary to obtain very low viscosity measurements. Heat loss from the tygon tubing and the metal adapter was considered. Measurements comparing the bath temperature with the thermocouple readout to the actual temperature of the liquor were collected and compiled to create a calibration chart for temperature references. In the tests requiring a temperature of 60°C for the liquid in

the UL adapter, the water bath was set at a temperature of 68°C to account for heat loss. Viscosity measurements were captured by streaming data from the viscometer to the computer program every five seconds. The data was averaged and the average viscosity was reported. Solids content was measured on all the black liquor samples using an instrument that heats up to 170°C and reports the solids content, expressed as a percentage, in a given volume of liquid. Specific gravity was measured using a hydrometer in the range of 1.0-1.2. The solids contents of TMP pressates were determined gravimeterically from a known volume of the liquid pressate that was freeze-dried. The residue was weighed and expressed as mg of residue per L of pressate.

### 2.5 Gas chromatography (GC) analysis

Individual extractives were quantified from the total extracted mass by gas chromatography using as Saturn 2000 GC equipped with an FID detector. The instrument operating conditions were

- Injector temp: 360°C
- Split mode: 50:1
- Injection volume: 1 uL
- Constant column flow: 1.6 mL/min, no pressure pulse

Oven temperature ramp: 110°C, 10°C/min to 190°C for 5 min, 2°C/min to 206°C for 2 min, 10°C/min to 265°C for 5 min, 5°C/min to 285°C for 5 min, 3°C/min to 312°C, 15°C/min to 360°C for 20 min. Total runtime: 75.10 min.

Freeze-dried samples were re-dissolved in acetone and volume giving about 10-15 mg/ml was transferred to a GC vial. The sample was blown down to dryness, re-dissolved in 1 ml of acetone, 10 mg of cholesterol was added as an internal standard, and the sample was methylated with diazomethane.

The compounds that were analyzed are presented in Table VII. A chromatogram demonstrating the resolution of the compounds in Table VII is present in Figure 2.

The samples used in this experiment include chip samples obtained from mills experiencing foaming issues and samples with a known time since mountain pine beetle death of approximately 1, 5, and 10 years. These chips were pulped to generate liquors for foaming studies. In addition to these mill chips, sample preparation modifications were used to add further diversity to the sample base by changing the applied effective alkali charge (EA) in order to affect the residual effective alkali (REA) of the black liquor samples. A varied sample base allows many different factors to be investigated when exploring the nature of foaming in black liquor samples. Figure 3 shows a selection of samples that were analyzed for extractives content. These chips were also analyzed for extractives content and profiles. Extractives content was determined using the acetone soluble extractives resulting from Soxlet treatment. The acetone samples from successive Soxlet treatments were combined and reduced in volume to the saturation point. A 1 mL sample of the soluble extractives was reduced to dryness and freeze-dried, and the gravimetric weight of the extractives in mg/mL was recorded.

Table VII. List of the extractives that were analyzed, grouped by class.

| Fatty Acids | Resin Acids | Sterols | Glycerides | | | Others |
|---|---|---|---|---|---|---|
| | | | Mono- | Di- | Tri- | |
| Palmitic acid | Pimaric acid | | Monostearin | 1,3-Dipalmitin | Trimyristin | Alcohols |
| Octadecanoic acid | Dehydroabietic | | Monopalmitin | 1,3 Distearin | Tripalmitin | 1-Docosanol |
| Linoleic acid | acid | β-sitosterol | | | Tristearin | |
| Oleic acid | Abietic acid | Stigmastanol | | | Trinonadecanoin | Esters |
| Stearic acid | Neoabietic acid | Stigmasterol | | | Tricaprin | C16 acid-stearyl ester |
| Stearolic acid | | | | | | C18 acid-stearyl ester |
| Heneicosanoic acid | | | | | | C20 acid-Stearyl ester |
| Tricosanoic acid | | | | | | |
| Tetrecosanoic acid | | | | | | |
| Betulin | | | | | | |

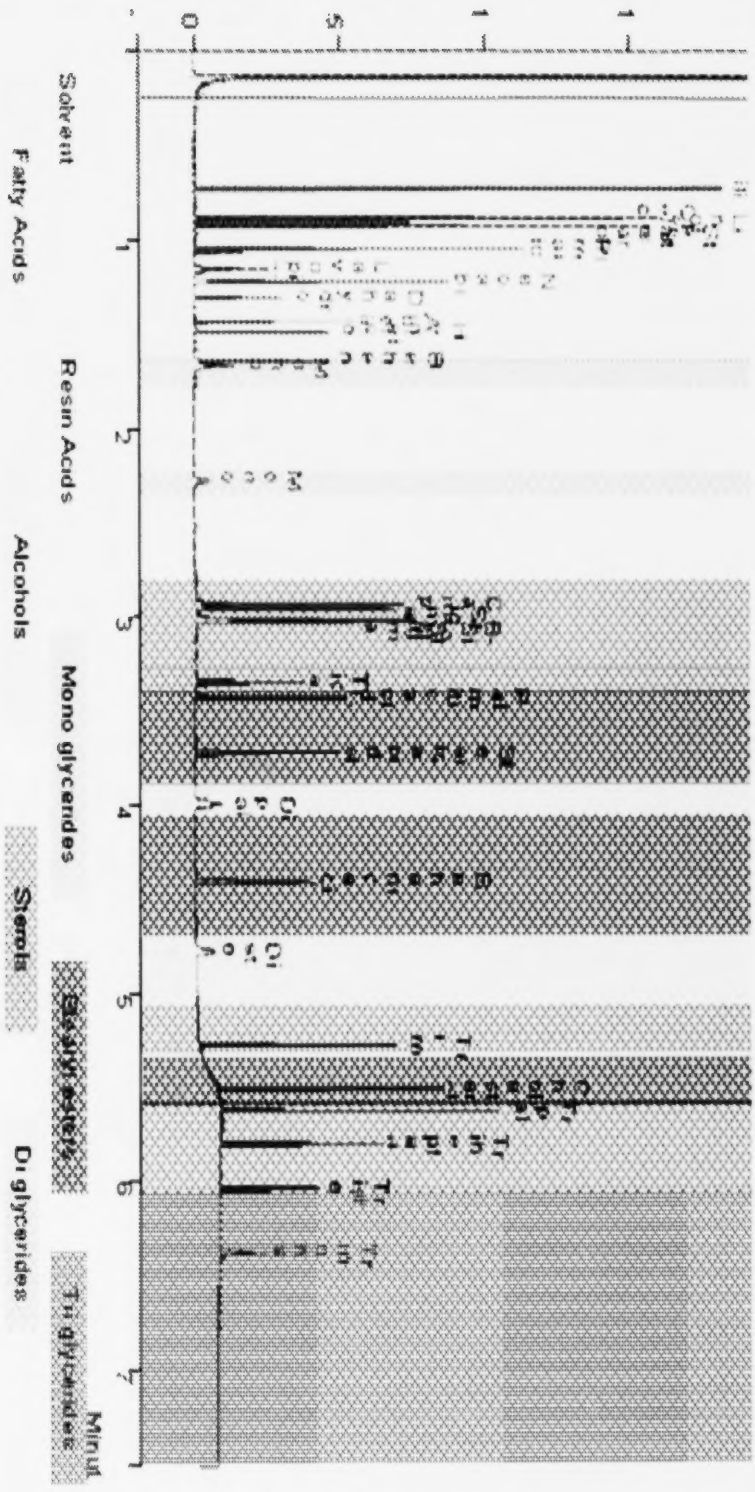


Figure 2. Sample Chromatogram of extractives (courtesy of B. Sithole, FPInnovation-Paprican).

## 2.6 Measurement of Foaming Propensity

Figure 3 shows a schematic view of the Foaming Propensity Apparatus used to measure foam dynamics. The system consists of a plexiglass tube (the foaming vessel) surrounded by a water jack. Temperature within the foaming vessel was maintained by circulating water that had been heated in water bath through the inlet and outlet ports of the water jacket. The liquid to be tested was placed into the foaming vessel and nitrogen gas (analytical grade) was bubbled through the liquid via a fritted sparger. Gas flow was controlled via a valve. The gas was vented through the top of the foaming vessel and bubbled through a solution of saturated ZnCl in order to trap sulphurous gases stripped from the liquids during the procedure. A tape measure was placed on the side of the foaming vessel to facilitate foam measurements. The volume of a liquid or foam in the foaming vessel can be calculated by the simple relationship: volume = $\pi r^2 h$. Where $r$ is the radius of the vessel (12.5 mm with this apparatus) and $h$ is the height of the liquid as read from the tape measure. Two such systems were set up in parallel to expedite the analysis, one solely for black liquors, the other for TMP pressates.

Prior to starting a foaming measurement, a known volume ($V_l$) of the liquid to be tested, either weak black liquor or TMP pressate, is introduced into the foaming vessel and the level of the liquid measured using the tape measure. Both the column and the liquid of interest are brought to the desired temperature for the test. To initiate a foaming measurement, nitrogen gas is introduced through the metal sparger, at a set flow rate, into a liquid sample (Figure 4). The agitation resulting from the gas causes the generation of a foam in the column. The height of the foam generated within a given period of time (typically less than 10 seconds), the change in the volume of the liquid ($V_{lf}$), and the time (in seconds) required for the foam to collapse, are recorded.

Foam density is defined as the amount of liquid in the foam and is calculated by multiplying the $V_{lf}$ by the $\rho$ (liquid density as calculated from its specific gravity) and dividing that by the volume of foam generated during the sparging process. Collapse time, an indicator of foam stability, is determined by timing the collapse of the foam from the cessation of gas flow to when the foam has returned to the liquid phase. In some cases, insufficient foams were generated under the conditions used in this study. In such instances, only the foam volume could be estimated. In all instances, the reported values for foam density and collapse time are the averages of five separate determinations.

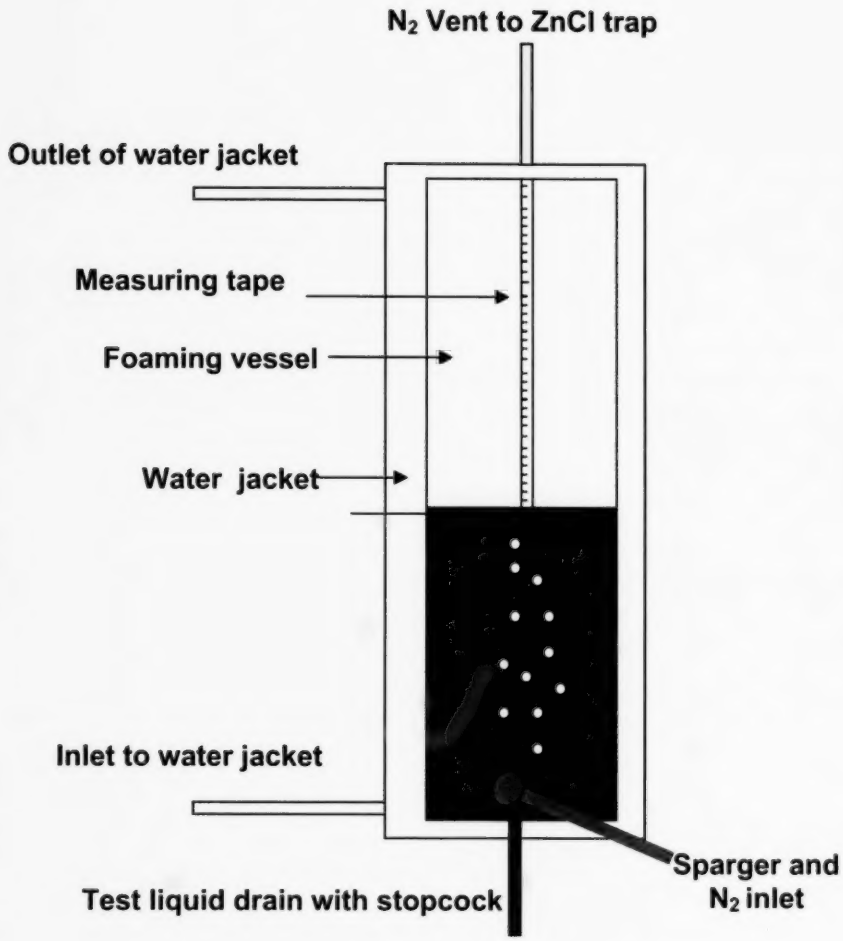


Figure 3. Schematic Diagram of the Foaming Propensity Apparatus

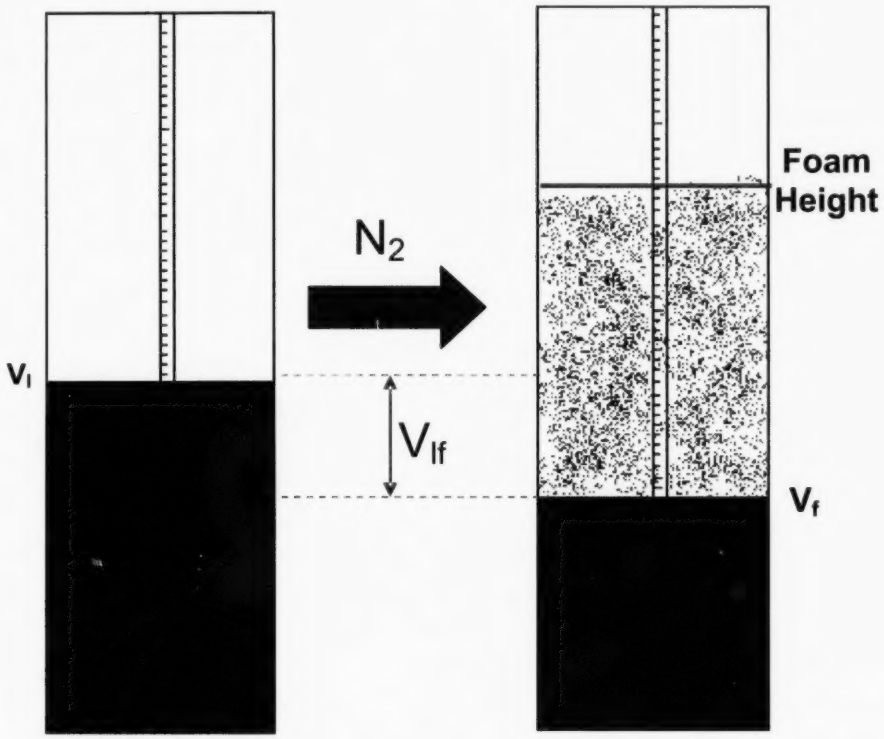


Figure 4. Schematic of the measurements used to calculate $V_{lf}$ , foam height measurement and foam density.

## 3 Results and Discussion

### 3.1 Influence of mountain pine beetle infestation on lodgepole pine extractives content and composition

The average total extractives content of the core samples was 2.8% (2.06% Std. Dev.), but results for individual cores were highly variable with values ranging from 0.7% to over 11%. While high in some instances, the total extractives levels were, on average, comparable to those reported in the literature (Table I). No significant differences (95% confidence interval) between total extractives and BEC site of growth were evident (Figure 5).

Gas chromatography was used to quantify the individual compounds (listed in Table VII) in the material extracted from each sample. These compounds were grouped into classes of fatty acids, resin acids, alcohols and sterols, which made up unsaponifiable type compounds, and the sterol esters, mono-, di- and tri- glycerides which comprised saponifiable-type compounds. Collectively, all of these compounds are considered as

lipophilic material and it was recognized that these compounds comprised only a portion of the total acetone extractives from each core. Difference between the masses of the total extractives and all identified lipophilic compounds was categorized as "unknown". This unknown fraction could include a wide range of compounds and may warrant further investigation, but, as this study was centered on the lipophilic compounds produced during the resinous response that are of industrial significance, further investigation of the "unknown" fraction is beyond the scope of this study.

Cores from the SBS zone had, on average, 1.07% (0.99% Std. Dev.) lipophilic extractives and those from the SBPS zone had 1.56% (1.05% Std. Dev.). The differences were statistically significant (t-test) and were also transformed into the "unknown" fraction. Therefore, trees from the SBS zone tend to have lower levels of lipophilic materials and higher levels of the "unknown" materials than trees from the SBPS zone.

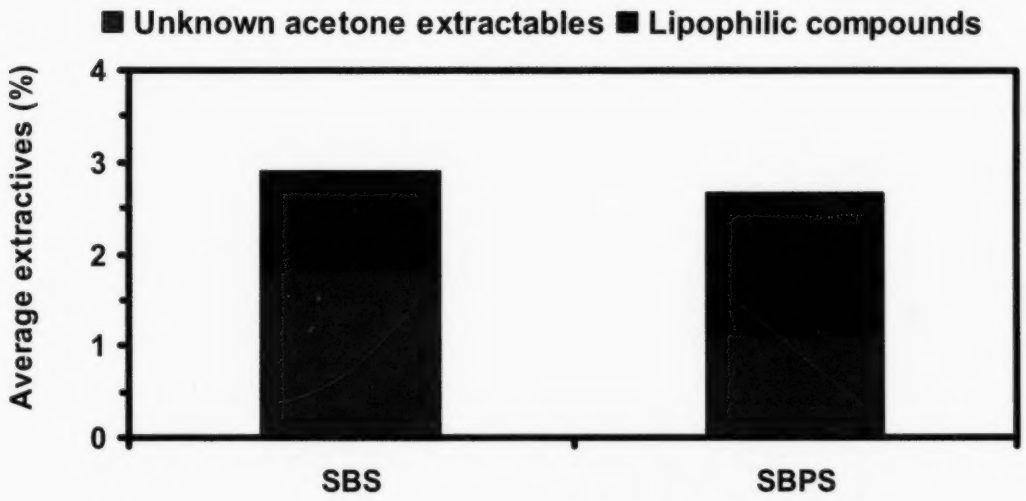


Figure 5. Lipophilic and "unknown" acetone extractables for lodgepole pines grown in either the SBS or the SBPS BEC zones. Each bar represents the average amount of total material extracted.

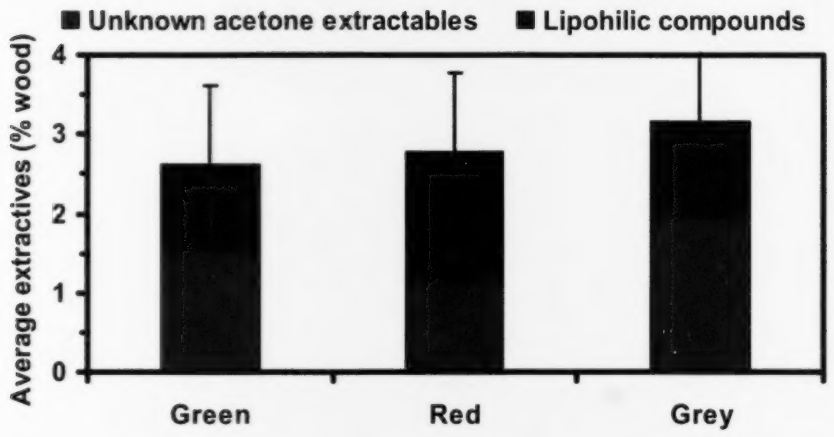


Figure 6. Lipophilic and "unknown" acetone extractables for lodgepole pines in green (unattacked), red, or grey stage of mountain pine beetle infestation. Each bar represents the average amount of total material extracted. Error bars are 1 standard deviation of the total extractives.

The total extractives, lipophilic material and unknown extractables, averaged by stage of mountain pine beetle wood (unattacked green, red, grey) are presented in Figure 6 and Table VIII. While there appears to be a trend towards higher average total extractives as wood progresses from green stage through to red and grey stages (Figure 6), a subsequent Analysis of Variation (ANOVA) did not show any significant differences between the total extractives contents of the three wood types for either BEC zone (Table VIII). Between-tree variability was too excessive, even within BEC zone or a specific site index, to allow for a firm conclusion on how extractives levels vary with respect to stage of mountain pine beetle infestation. A more appropriate strategy may be to follow the extractives profiles of individual trees over time, typically 5 years or longer. This approach has been successfully used by Shrimpton [28], but for shorter time periods – of 2 years and less – than considered in this study.

The effect of mountain pine beetle infestation on the composition of the lipophilic material that was extracted by acetone is presented, by class as a percentage of the mass lipophilic fraction, in Figure 7 and, in more detail, in Table VIII. In this table, data is expressed as mass of compounds per mass of wood. A cursory examination of the extractives profiles shows that resin and fatty acids make up between 85%-95% of the lipophilic fraction. Sterols, sterol esters and glycerides make up most of the remaining 5%-15% of the lipophilic fraction. This is consistent for all stages of mountain pine beetle infestation (Fig. 7). A more detailed examination with the goal of identifying trends between compound classes with beetle infestation is presented in Table VIII. The proportion of free acids reported in this study are consistent with that reported for sound lodgepole pines (Table I). Therefore, these results tend to agree with the observation that the extractives profiles of mountain pine beetle-infested wood differ from those of unattacked (green) wood.

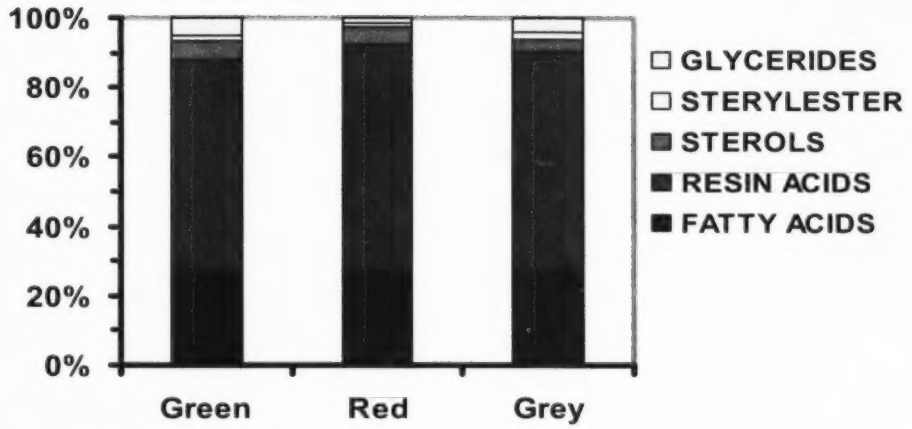


Figure 7. Percent composition of the lipophilic fractions for each of the three stages of mountain pine beetle-killed wood. Average lipophilic content of each stage: Green (unattacked) .09%(Std. Dev. 1.06%), Red 1.62% (Std. Dev. 1.01%), Grey 1.21% (Std. Dev. .96%).

Table VIII. Average total extractives -- expressed as % on wood, lipophilic and unknown extractables composition for unattacked-green, red and grey stage woods. Standard deviations are given in brackets. Also, the proportion of total extractives assigned to specific compound classes is presented -- expressed as mg/kg of dry wood. N.B. 1% = 10,000 mg/kg MPB = mountain pine beetle

| | MPB attack stage of wood | | |
|---|---|---|---|
| | Green-unattacked | Red | Grey |
| n | 43 | 29 | 25 |
| Expressed as % of wood mass | | | |
| Total extractives | 2.64 (2.01) | 2.77 (2.13) | 3.16 (2.13) |
| Min | 0.8 | 0.7 | 1.1 |
| Max | 11.5 | 9.2 | 10.5 |
| | | | |
| Lipophilic extractives | 1.09 (1.06) | 1.62 (1.01) | 1.21 (0.97) |
| Unknown extractives | 1.53 (1.57) | 1.16 (1.32) | 1.95 (1.40) |
| | | | |
| Expressed as mg/kg of dry wood | | | |
| Fatty Acids | 3142 (324) | 2132 (402) | 4345 (425) |
| Resin Acids | 9343 (1502) | 6883 (1861) | 13088 (1969) |
| Alcohols | 72 (12) | 63 (15) | 98 (16) |
| Sterols | 101 (13) | 166 (17) | 196 (18) |
| Sterol Esters | 130 (26) | 76 (33) | 207 (34) |
| Total Glycerides | 5.2 (0.5) | 2.3 (0.5) | 4.8 (0.6) |

Table IX. Analysis of Variance (ANOVA) were performed on Log transformed concentrations and correlated with mountain pine beetle stage of attack (green-unattacked, red, or grey) and BEC zone (SBS, SBPS). $R^2$ represents the squared multiple regression coefficient (proportion of variation within an extractive constituent assigned to the two factors). Boldface text in the F-ratio column indicates that the *p*-value for that factor (mountain pine beetle stage or BEC) is less than 0.050 and, therefore, that there is a statistically significant relationship between the corresponding factor(s) and the concentration of a specific class of compounds. The η indicates the proportion of variability ($R^2$) explained by the corresponding factor. MPB = mountain pine beetle

| | $R^2$ | Factor | Mean -Square | F-Ratio | H |
|---|---|---|---|---|---|
| Fatty Acids | 0.233 | MPB | 0.427 | **2.946** | 16% |
| | | BEC | 2.131 | **14.700** | 79% |
| | | Error | 0.145 | | |
| Resin Acids | 0.208 | MPB | 0.582 | **2.793** | 14% |
| | | BEC | 3.332 | **16.006** | 81% |
| | | Error | 0.208 | | |
| Alcohols | 0.077 | MPB | 0.268 | 1.205 | 20% |
| | | BEC | 0.869 | **3.903** | 64% |
| | | Error | 0.223 | | |
| Sterols | 0.158 | MPB | 1.107 | **8.748** | 75% |
| | | BEC | 0.249 | 1.966 | 17% |
| | | Error | 0.127 | | |
| Sterol Ester | 0.247 | MPB | 0.771 | **3.337** | 19% |
| | | BEC | 3.055 | **13.212** | 75% |
| | | Error | 0.231 | | |
| Glycerides | 0.271 | MPB | 0.039 | 0.423 | 3% |
| | | BEC | 1.304 | **14.134** | 91% |
| | | Error | 0.092 | | |

It is difficult to identify trends between the stage of mountain pine beetle-affected wood and extractives profiles, expressed as classes of compounds, based on the information presented in Table VIII. Site effects and inherent variation between trees can still influence extractives levels to a great extent. Analysis of variance (ANOVA) was used to determine the extent of the influence that stage of beetle infestation, site of growth and other factors have on the classes of compounds (Table IX). The two factors are time since mountain pine beetle infestation (green, red, grey) and BEC site of growth (SBS, SBPS). No significant interactions between the mountain pine beetle and BEC factors on the different compound classes were noted and, therefore, only the effects of individual factors are reported.

The results presented in Table IX highlight the interrelationship between the stage of mountain pine beetle infestation and the site from where the individual trees originate, for the six compound classes examined. In four out of the six classes examined, which represented over 90% of the lipophilic extractables, correlation coefficients ($R^2$) ranged from 0.208 to 0.271. The $R^2$ for the other classes, which represented less than 5% of the lipophilic extactables, were less than 0.200. This indicates that 70%-90% of the variability in the six classes of extractives is not explained by either mountain pine beetle or BEC. Of the 20%-30% of the variability that is explained by these two factors, most is explained by the site factor. However, the mountain pine beetle factor does significantly affect four of the six classes to some degree. Most notably are the predominant resin and fatty acids, and, interestingly, the sterols where the mountain pine beetle factor accounts for about 75% of the variability.

One final point on the effect of BEC zone on extractives levels. The 41 sites sampled in the SBS zone for this study tended to be drier than the 57 sites sampled in the SBPS zone (Table X). Trees from the SBS zone tend to have significantly lower levels of lipophilic extractables than trees from the SBPS zone. This suggests that the moisture profile of the site influences the extractives levels of trees. The dataset used in this study could not be used to confirm this. A targeted study with a more balanced design with respect to site moisture profiles would be required to investigate this phenomenon further.

The results presented in Tables III and IV are consistent with the results presented in this study (Figure 6, Table VIII), namely an initial (green-unattacked to red stage) increase in lipophilic extractives due to the *de novo* synthesis of acetone extractable compounds. The higher levels of lipophilic extractives noted in the cores from the grey and advanced grey pine trees, particularly in trees from the SBS zone, are not attributed to synthesis of new materials as the trees in these stages of mountain pine beetle infestation are dead. As there was no evidence of decay which could account for the synthesis of fatty acids and sterols by wood degrading fungi, it is concluded that these higher levels of extractives are the remnants of high levels of extractives in these trees at the time of infestation or very shortly after. The fact that these compounds have been preserved, in some cases for 8 to 15 years, in dead standing trees is remarkable.

Attempts to correlate extractives profiles with time-since-death were unsuccessful. Therefore, Partial Least Squares-Discriminant Analysis (PLS-DA) was used to determine if the individual compounds in Table VIII could be used to classify wood samples into the green, red, or grey stages of mountain pine beetle infestation. Two models are presented; both used the log transformations of the concentrations (as mg /kg of oven-dried wood) of each component (listed in Table VII). All log transformed data were mean centered and variance scaled. Also, a single point, point 34, was determined to be an outlier and was omitted from further investigations.

In order to determine the impact of site on the extractives profiles, the site index was included as a variable in model I but was excluded in model II. In both models, any trees that had been dead longer than 4 years were considered "grey", trees that had been dead between 2-4 years (inclusive) were classified as "red", and all other trees were classified as "green". The two PLS-DA models are summarized in Table X.

Table X. Summary of the two PLS-DA models including the components and the cumulative variance explained in the X (log of extractives levels) variables ($R^2X$), the variance explained in the Y variables (green-unattacked, red, or grey class).

| | Components | $R^2X$ (cumulative) | $R^2Y$ (cumulative) | $Q^2$ (cumulative) |
|---|---|---|---|---|
| Model I -BEC included | 3 | 0.806 | 0.383 | 0.244 |
| Model II- BEC excluded | 3 | 0.798 | 0.352 | 0.181 |

Table X shows that Models I and II account for 80% and 81% of the variability in the X data sets, respectively (log of the extractives concentration based on wood). Both models account for between 38% and 35% of the variance observed in the Y data set (mountain pine beetle stage). However, the $Q^2$ -value, an indicator of the robustness of a model, dropped when BEC data was excluded (from 0.244 to 0.181). This is consistent with earlier observations that much of the variability noted in the extractives profiles of pines can be related to site as well as mountain pine beetle infestation. Despite this improvement, the $Q^2$ –value was still considered low, and the predictive capabilities of the models may be limited. The loading plots for both models are presented in Figures 8 and 9.

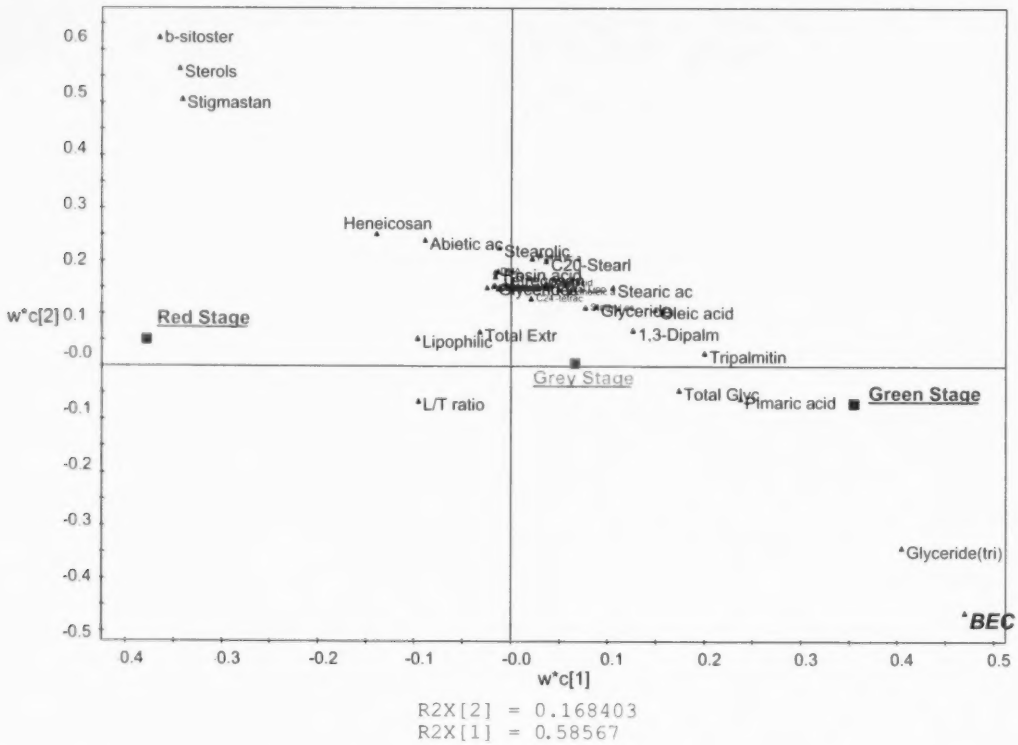


Figure 8. Loading plot for the first two components of model I – BEC included (Table X). Together, these components account for over 75% of the variability of X. The mountain pine beetle stages are also indicated. The influence of BEC is emphasized in the figure for discussion purposes.

The loading plots show relationships between the extractives content with the stage of mountain pine beetle infestation for models I and II (with and without the BEC variable). Firstly, the loading plots for both models are very similar. For both models, most of the variability in the extractives profile is captured in component 1. While little variability in the mountain pine beetle stage data set (the Y data set) is captured in component 2, most of this variation is related to component 1. Interestingly, the position of the green and grey stages relative to each other along the component 1 axis suggests that the extractives profiles of these two types of wood are more similar to each other than to that of the red stage wood.

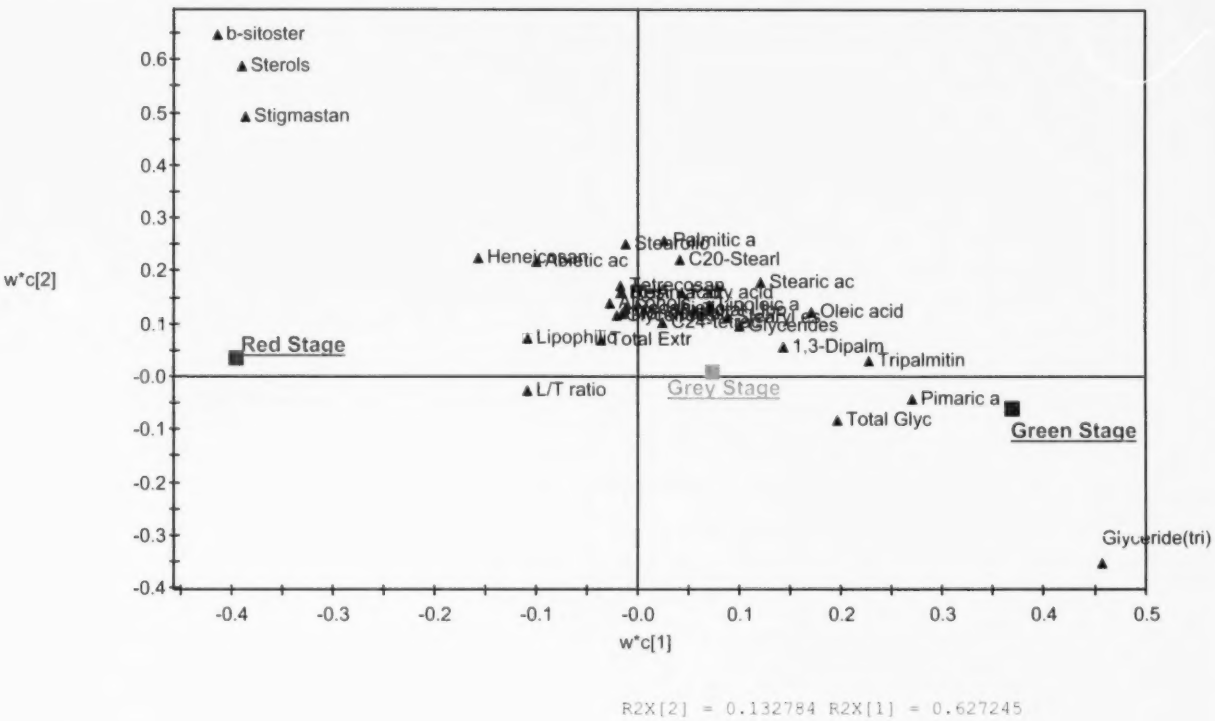


Figure 9. Loading plot for the first two components of model II- BEC excluded (Table X). Together, these components account for over 75% of the variability of X. The mountain pine beetle stages are also indicated.

No clear indication of how changes in total extractives content or the levels of lipophilic extractables relate to mountain pine beetle infestation was evident. Other factors, such as tree to tree and within-tree variability, must affect these parameters. From the loadings plot of model I (Figure 8), it is evident that the triglycerides levels are positively correlated with site of growth (BEC zone), highlighting the site-specific nature of these

types of extractives. While total glycerides levels (including mono-, di- and tri-) were positively correlated with the unattacked green stage, no individual glycerides were correlated with levels of infestation. It would seem that glyceride production is curtailed in response to mountain pine beetle infestation. In contrast, free sterols such as β-sitosterol and stigmastanol, were highly correlated with the red stage of infestation. Other extractives classes, such as free fatty acids and resin acids, did not vary with mountain pine beetle infestation. The sole exception was pimaric acid which was negatively correlated with the red stage wood (Figures 8 and 9).

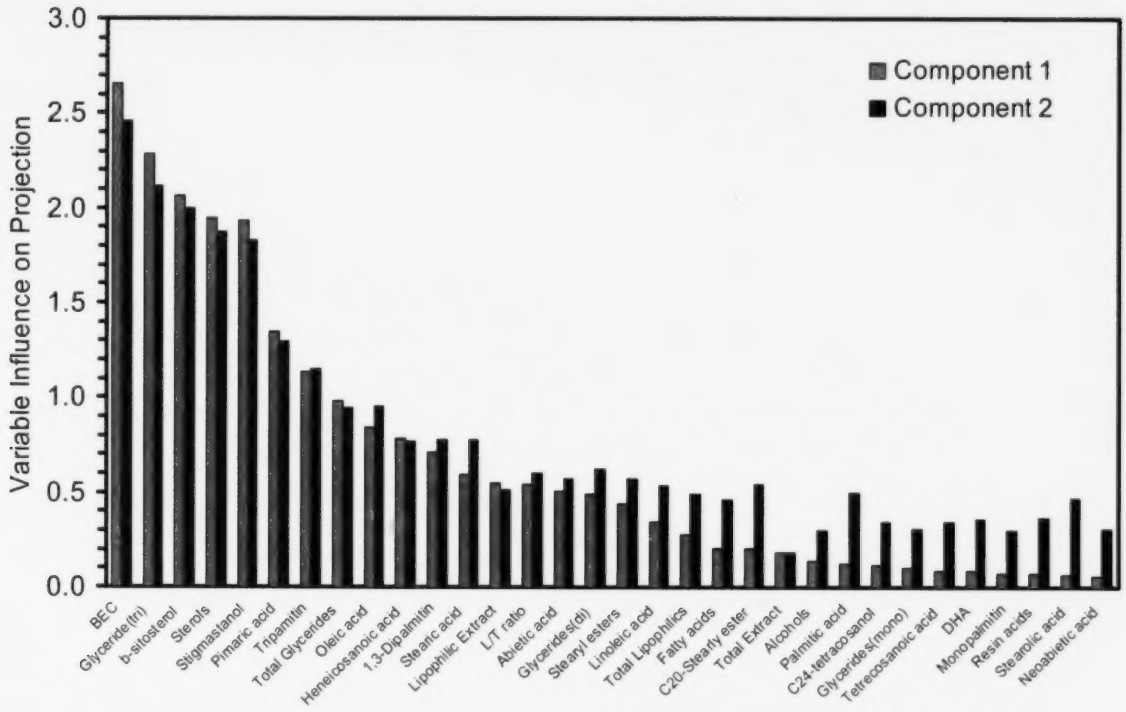


Figure 10. Influence of variable on components 1 and 2 for model I (BEC included). The higher the "VIP" value, the greater the influence of the variable on the respective component.

The influence of different types of extractives on components 1 and 2 for model I (BEC included) and model II (BEC excluded) are presented in Figures 10 and 11, respectively. The higher the variable influence on projection (VIP) presented, the greater influence that factor has on the respective component. Investigation of the "VIP" plot for model I shows that site (BEC) has the strongest influence on components 1 and 2 (Figure 10). If this variable is excluded (Figure 11), the main variables that influence the first two components in the models (which account for over 75% of the total variance) are, in descending order: triglycerides, β-sitosterol, total sterols, stigmastanol, pimaric acid, tripalmitin, and total glycerides. Other mono-, di- and triglycerides, as well as some free fatty acids (notably oleic acid), also had a strong impact on the two components. The

impact of resin acids such as abietic acid and dehydroabeitic acid (DHA) were relatively minor, in spite of the fact that these account for most of the resin acids present in the extracts.

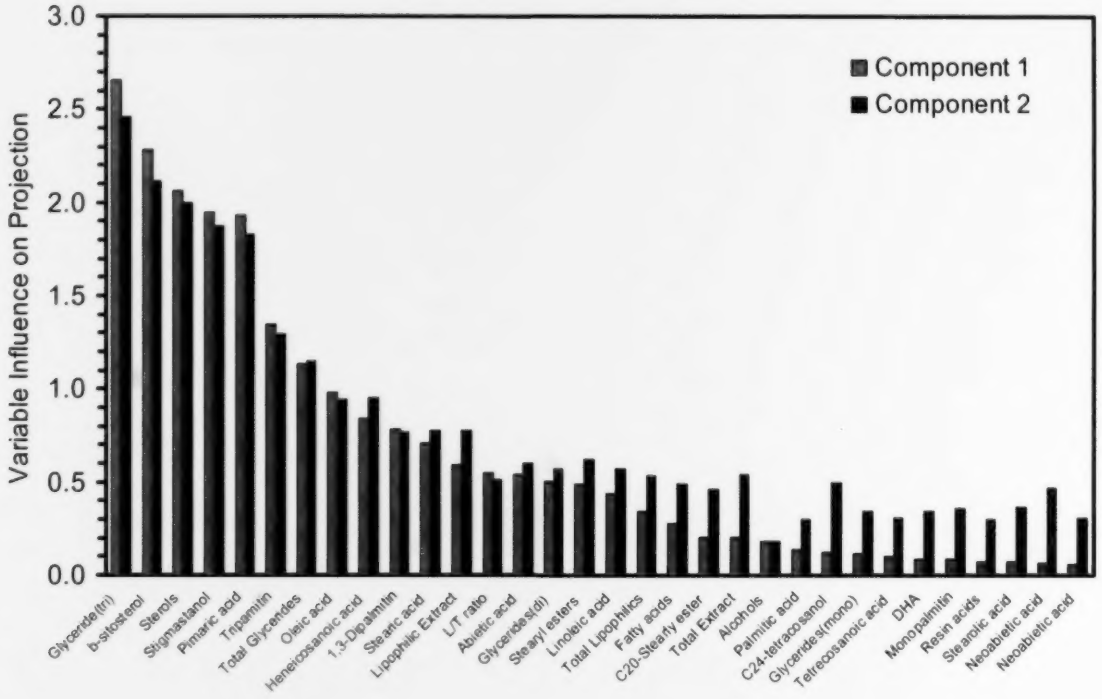


Figure 11. Influence of variable on components 1 and 2 for model II (BEC excluded). The higher the "VIP" value, the greater the influence of the variable on the respective component.

In general, the results obtained for resin and fatty acids are consistent with those reported by Shrimpton in Table III. Specifically, levels of abietic acid types of resin (abietic and DHA) and total free fatty acids were relatively unaltered by mountain pine beetle infestation. In this study, variability in pimaric acid levels was linked with mountain pine beetle infestation, while in the Shrimpton study (Table III) it was noted, but not necessarily linked, with mountain pine beetle infestation. The Shrimpton study did not report glycerides directly but did show significant variability in the fatty acids released after saponification (Table III). While most of the fatty acids came from glycerides, it is recognized that other fatty acid esters could also contribute to this variance. In this study, the main impact of mountain pine beetle was on glyceride levels which were negatively correlated with red stage attacked wood, and sterols which were positively correlated with this type of wood. Whether this drop in glycerides levels is due to a cessation of *de novo* glyceride synthesis by the tree, degradation by bluestain fungi [42], or abiotic decomposition is unclear.

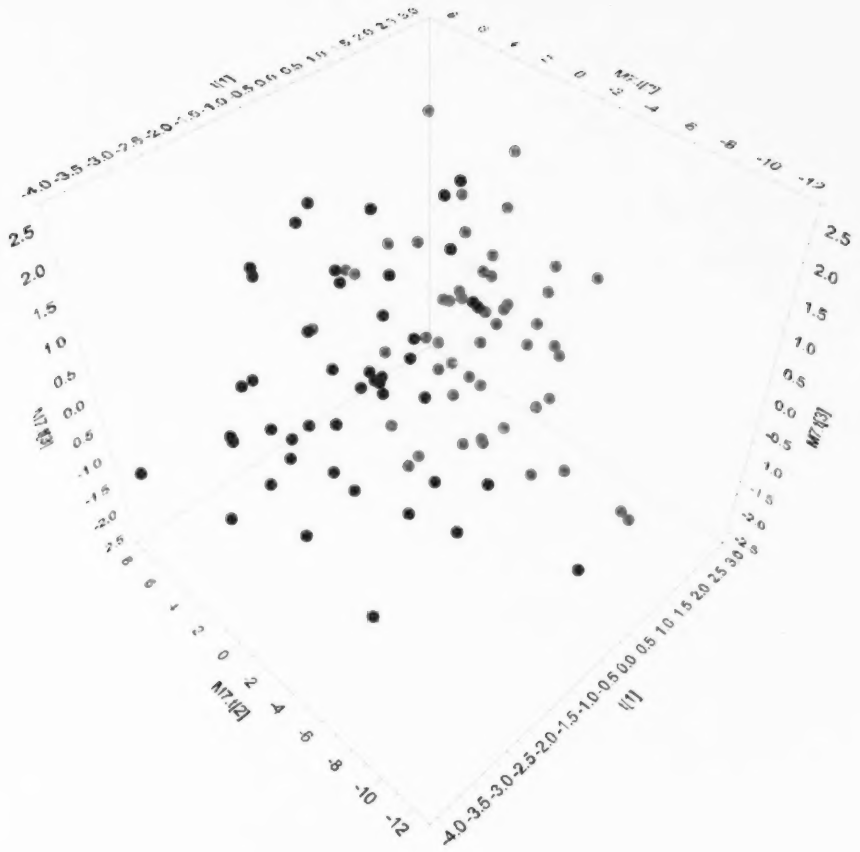

Figure 12. 3-D scatter plot of scores for the green, red and grey t-values for the samples used in model I (BEC included).

The ability of the PLS-DA models to differentiate between the unattacked-green, red and grey stage wood, based on extractives profiles from the cores used to construct the models, are presented in Figures 12 and 13, for models I and II, respectively. In these figures, it is evident that the unattacked-green and the red stage woods tend to cluster separately, mainly within the t[1] and t[2] space. The grey stage wood samples, which appear to cluster with the unattacked-green wood, tend to separate from this class along the t[3] axis. Therefore, even with some overlap, it is evident that the PLS-DA models can be used to classify the cores used in this study to assess whether the trees had been attacked by mountain pine beetle or not.

It would be advantageous to use model II (BEC excluded) because detailed site information is often not readily available for most wood samples, particularly chip

samples. Furthermore, it seems from Table X and comparing Figures 12 and 13, that while the BEC does account for some variability, significant amounts of the variance (over 75%) are accounted for by the chemical components of the extractives. In order to determine if BEC is needed, the coefficients for both models I and II were compared via paired t-test and the $R^2$ determined for green I/green II, red I/red II, and grey I/grey II pairs of data sets. The one coefficient omitted was for BEC, as there was no corresponding value in the model II coefficient matrix. In all three pairs of coefficients matrices, there were no significant differences between the model I and the model II coefficient matrices. Also, the $R^2$ were 0.99 or greater, indicating that the two matrices for models I and II were very similar. Therefore, from this point on, only model II is considered. The coefficients for this model are presented in Table XI.

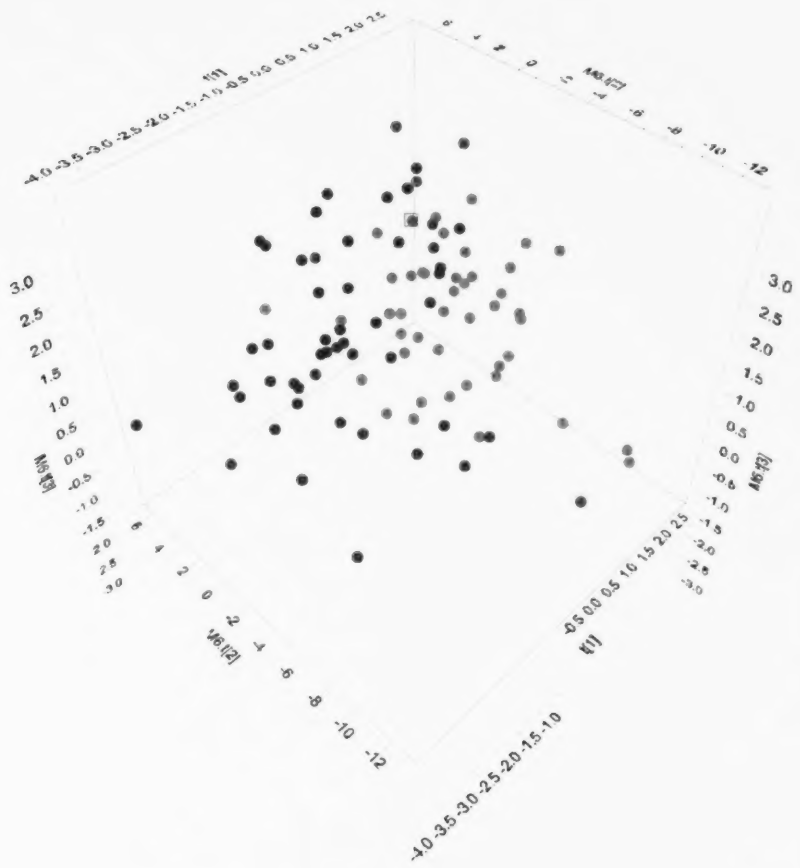

Figure 13. 3-D scatter plot of scores for the green, red and grey t-values for the samples used in model II (BEC excluded).

The model II coefficients presented in Table XI, were ordered and plotted in Figure 14, which presents the data in a manner analogous to the loadings plot (Figure 9). We can see that in the red stage wood, sterols are expected to be higher and triglycerides lower than in unattacked wood, while grey stage wood is expected to be fairly consistent in extractives patterns, relative to the other two classes of wood. Figures 12 and 13 show that the t-scores generated by each model can be used to group the calibration data into green, red, or grey classes. From the chromatographic profile of the acetone extractives of a lodgepole pine sample, with individual compounds or classes of compounds expressed and log transformed as indicated in Table XI, unattacked-green, red and grey values can be calculated. These are obtained by multiplying the transformed data for each constituent with the corresponding coefficient for each mountain pine beetle class, then summing the values within a class. The sample is assigned to the class with the highest value. Samples are expected to be correctly assigned about 80% of the time, according to Table X, if the model is robust enough for use.

Table XI. Coefficients for models II as outlined in Table X.

| | Units prior to transformation | Log | Green II | Red II | Grey II |
|---|---|---|---|---|---|
| Constant | NA | NA | 0.896 | 0.954 | 0.279 |
| Total Extracts | % | Yes | -0.013 | 0.014 | -0.002 |
| Lipophilic Extracts | % | Yes | -0.040 | 0.044 | -0.007 |
| L/T ratio | Unitless | No | -0.039 | 0.043 | -0.007 |
| Site Index | Unitless | No | NA | NA | NA |
| Palmitic acid | mg/kg wood | Yes | 0.009 | -0.010 | 0.002 |
| Linoleic acid | mg/kg wood | Yes | 0.025 | -0.028 | 0.005 |
| Oleic acid | mg/kg wood | Yes | 0.062 | -0.068 | 0.012 |
| Stearic acid | mg/kg wood | Yes | 0.044 | -0.048 | 0.008 |
| Stearolic acid | mg/kg wood | Yes | -0.005 | 0.005 | -0.001 |
| Pimaric acid | mg/kg wood | Yes | 0.098 | -0.108 | 0.018 |
| DHA | mg/kg wood | Yes | -0.007 | 0.007 | -0.001 |
| Abietic acid | mg/kg wood | Yes | -0.037 | 0.040 | -0.007 |
| eoabietic acid | mg/kg wood | Yes | -0.004 | 0.005 | -0.001 |
| Heneicosanoic acid | mg/kg wood | Yes | -0.058 | 0.063 | -0.011 |
| Monopalmitate | mg/kg wood | Yes | -0.006 | 0.006 | -0.001 |
| C24-tetracosanoic acid | mg/kg wood | Yes | 0.009 | -0.009 | 0.002 |
| Tetrecosanoic acid | mg/kg wood | Yes | -0.007 | 0.007 | -0.001 |
| b-sitosterol | mg/kg wood | Yes | -0.151 | 0.165 | -0.028 |
| Stigmastanol | mg/kg wood | Yes | -0.141 | 0.154 | -0.026 |
| 1,3-Dipalmitate | mg/kg wood | Yes | 0.052 | -0.057 | 0.010 |
| C20-Stearloate | mg/kg wood | Yes | 0.015 | -0.016 | 0.003 |
| Tripamitin | mg/kg wood | Yes | 0.083 | -0.091 | 0.016 |
| Fatty acid | mg/kg wood | Yes | 0.015 | -0.017 | 0.003 |
| Resin acid | mg/kg wood | Yes | -0.005 | 0.006 | -0.001 |
| Alcohols | mg/kg wood | Yes | -0.010 | 0.011 | -0.002 |
| Sterols | mg/kg wood | Yes | -0.142 | 0.155 | -0.027 |
| Stearyl ester | mg/kg wood | Yes | 0.032 | -0.035 | 0.006 |
| Glycerides (mono-) | mg/kg wood | Yes | -0.007 | 0.008 | -0.001 |
| Glycerides (di-) | mg/kg wood | Yes | 0.036 | -0.040 | 0.007 |
| Glyceride (tri-) | mg/kg wood | Yes | 0.167 | -0.182 | 0.031 |
| Total Lipophilic Extr | mg/kg wood | Yes | 0.020 | -0.022 | 0.004 |
| Total Glycerides | mg/kg wood | Yes | 0.072 | -0.078 | 0.013 |

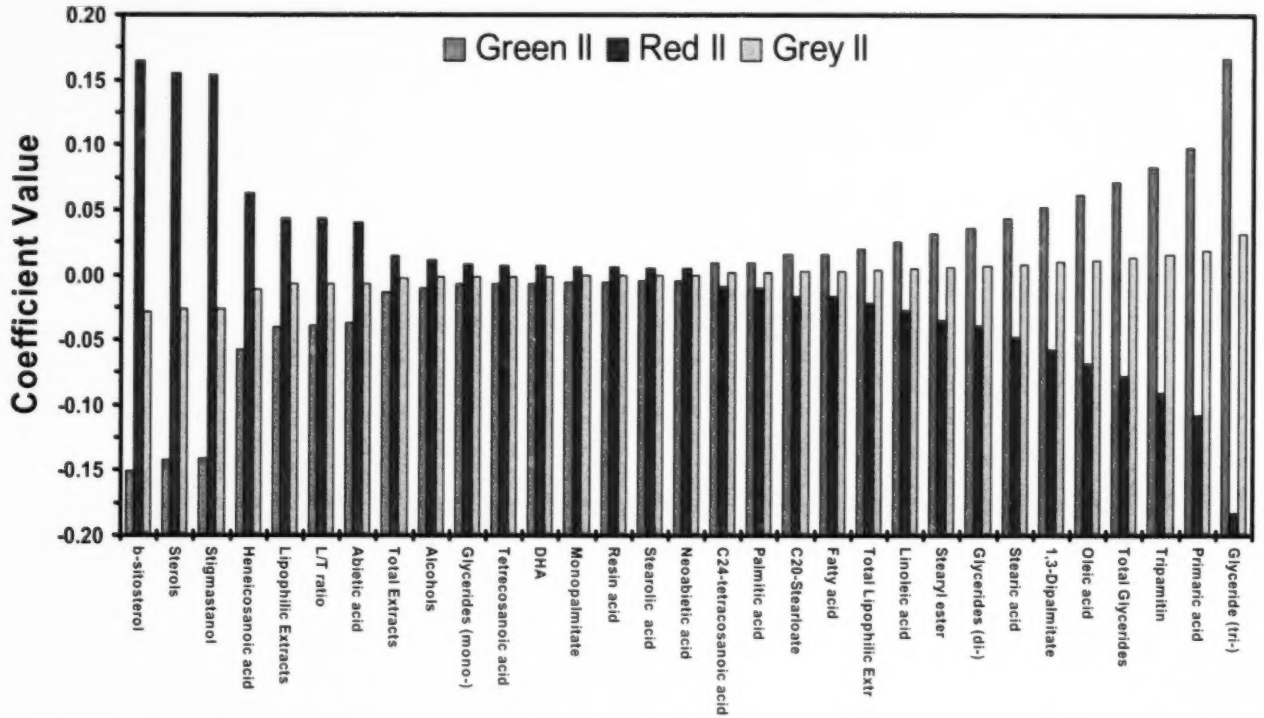


Figure 14. Comparison of the coefficients for the three PLS- DA classes (green, red, and grey) for each constituent. BEC was excluded.

In order to determine how robust the model is, a validation set consisting of acetone extracts from chips from both mill samples and mature lodgepole pine wood samples from trees infested with mountain pine beetle, was evaluated. These extracts were analyzed via GC and the ensuing data was processed as previously described. The extractives data from these chip samples were log transformed (as per Table XI), scaled and centered, and run through the PLS-DA model via SIMCA-P+ 11.0. This software package generated several parameters, including membership probabilities and distance to models in X space (DMS).

Prediction of capabilities of PLS-DA models for the classification of wood chips as "green", "red" or "grey" was tested on chips that came from mills [5] or from known pines samples chipped as per Dalpke et al.[69]. Results of the predictions are summarized in Table XII. The membership probability is a probability of whether an observation belongs to the model; any value that is less than 0.050 ($\alpha$ value) is not well described by the model. The DModX value is a combined measure of the residual standard deviation and the t-scores, and is used to assess how well a given data point fits the model. For this data set, points that have DModX values greater than 1.3 are not well represented by the model. Those with DModX values greater than 2 are considered outliers.

Of the 35 individual samples used for mountain pine beetle predictions, 19 corresponded to the mountain pine beetle class estimates, indicating that the PLS-DA model had an accuracy of 54% (Table XII). This is significantly lower than the expected 80%, as specified in Table X, and indicates that the model is not robust enough to reliably classify unknowns. There are several factors that contribute to these inaccuracies, but before these are explored, we should consider some aspects where the model behaved correctly. Firstly, there was one mill sample that was all hemlock and true fir with no pine at all (Table XII). The model was able to identify this sample as an extreme outlier, as indicated by the extremely low membership probability and the relatively high DModX value. In those samples that were done in replicate, the agreement within a replicate was considered good. Only one sample had one replicate that did not agree with the others within that set. This suggests that the methodology is precise, albeit inaccurate in classifying unknowns.

The deficiencies of the PLS-DA model are highlighted by the low membership probabilities for the mill chip samples, typically 0.100 or less. However, the membership probabilities of the lab chips, which were produced from the mature wood of trees that were cored for this study, were relatively high (greater than 0.700). In many cases these data fit the model very well, with probabilities greater than 0.900. This suggests that site of growth, which was unavailable for the mill chip samples, influenced the predictive capacity of the model. Other factors that affected the classification of mill chip samples included greater errors associated with the mountain pine beetle classification, wood species other than pine made up a significant proportion of the mill chip samples, and the storage conditions (known to affect extractives profiles) of the chips were uncertain. All of these factors contribute to the uncertainty of the PLS-DA models. It is very likely that other factors also contribute to this uncertainty. The models were also unable to

accurately classify the lab chip samples, despite the high membership probability values. This may be due to differences in the extractives profiles of cores and chips due to chipping or other factors. Therefore, the PLS-DA models developed in this study track extractives profiles in mountain pine beetle-infested pines from select BEC zones and can be used for this purpose. However, they are not considered robust enough to classify pine chips of unknown pedigrees as unattacked-green, red or grey stage wood.

Table XII. Prediction of capabilities of PLS-DA models for the classification of wood chips as "unattacked-green", "red", or "grey". Chips came from mills [5] or from known pines samples chipped as per [69]. Lab chip samples correspond to trees cores used in model development. mountain pine beetle estimates were presented in these references. The membership probability, DModX and predicted green, red, and grey values were generated from the PLS-DA model II by Simica-P+11.0. Mountain pine beetle attack stage predictions in boldface concur with the mountain pine beetle estimates. The chips obtained from the mills were extracted and analyzed in triplicate. Lab chip samples were analyzed singly. MPB = mountain pine beetle

| Origin | % Pine | MPB estimate | Membership prob. | DModX | Predicted Green - unattacked | Red | Grey | MPB predicted |
|---|---|---|---|---|---|---|---|---|
| | | | 0.008 | 1.52513 | 0.36564 | 0.40263 | 0.23173 | red |
| mill | 85 | green | 0.004 | 1.55994 | 0.42225 | 0.39502 | 0.18273 | **green** |
| | | | 0.002 | 1.62087 | 0.50210 | 0.34187 | 0.15603 | **green** |
| | | | 0.011 | 1.45746 | 0.19023 | 0.67200 | 0.13775 | **red** |
| mill | 40 | red | 0.013 | 1.43842 | 0.15423 | 0.73417 | 0.11161 | **red** |
| | | | 0.085 | 1.25187 | 0.25763 | 0.65485 | 0.08752 | **red** |
| | | | 0.006 | 1.4997 | 0.22972 | 0.63442 | 0.13579 | **red** |
| mill | 70 | red | 0.072 | 1.26794 | 0.28549 | 0.61294 | 0.10160 | **red** |
| | | | 0.107 | 1.22313 | 0.37155 | 0.53106 | 0.09739 | **red** |
| | | | 0.049 | 1.31863 | 0.18695 | 0.73689 | 0.07616 | red |
| mill | 70 | grey | 0.043 | 1.32948 | 0.29973 | 0.68444 | 0.01584 | red |
| | | | 0.034 | 1.34931 | 0.39323 | 0.53971 | 0.06706 | red |
| | | | 0.147 | 1.18673 | 0.10616 | 0.85143 | 0.04241 | red |
| mill | 70 | grey | 0.039 | 1.33245 | 0.06598 | 0.93166 | 0.00236 | red |
| | | | 0.261 | 1.10751 | 0.25183 | 0.72007 | 0.02810 | red |
| | | | 0.001 | 1.86249 | 0.16706 | 0.61297 | 0.21998 | **red** |
| mill | 85 | red | 0.001 | 1.76113 | 0.25050 | 0.54240 | 0.20706 | **red** |
| | | | 0.001 | 1.67067 | 0.36334 | 0.48620 | 0.15046 | **red** |
| | | | 0.000 | 2.85933 | -0.2104 | 1.06284 | 0.14754 | **other** |
| mill | 0 | other | 0.000 | 2.79204 | -0.2319 | 1.12383 | 0.10806 | **other** |
| | | | 0.000 | 2.77610 | -0.2674 | 1.21268 | 0.05467 | **other** |
| | | | 0.002 | 1.63970 | 0.08126 | 0.80260 | 0.11614 | red |
| mill | 70 | grey | 0.018 | 1.41638 | 0.20126 | 0.73811 | 0.06064 | red |
| | | | 0.032 | 1.35635 | 0.28561 | 0.68335 | 0.03105 | red |
| | | | 0.025 | 1.37980 | -0.00300 | 0.88404 | 0.11886 | **red** |
| mill | 70 | red | 0.006 | 1.50523 | 0.00662 | 0.88239 | 0.11099 | **red** |
| lab | 100 | green | 0.945 | 0.75264 | 0.73650 | 0.05998 | 0.20357 | **green** |
| lab | 100 | green | 0.788 | 0.86571 | -0.05385 | 1.01565 | 0.03820 | red |
| lab | 100 | green | 1.000 | 0.38572 | 0.88793 | 0.01724 | 0.09483 | **green** |
| lab | 100 | red | 0.699 | 0.91021 | -0.12680 | 1.06454 | 0.06226 | **red** |
| lab | 100 | red | 0.996 | 0.61821 | 0.40567 | 0.31022 | 0.28411 | green |
| lab | 100 | grey | 0.999 | 0.53374 | 0.09673 | 0.74437 | 0.15890 | red |
| lab | 100 | grey | 0.999 | 0.50496 | 0.55150 | 0.45410 | -0.0056 | green |
| lab | 100 | grey | 0.991 | 0.65422 | 0.34449 | 0.41369 | 0.24182 | red |
| lab | 100 | grey | 0.997 | 0.60186 | 0.33072 | 0.38532 | 0.28397 | red |

## 3.2 Effects of mountain pine beetle on foaming propensity during pulping

With an increase in the amount of mountain pine beetle-killed pine being pulped in BC by both kraft and mechanical mills, it has been observed that there has been an increase in the incidence of excessive foaming at various points during the pulping process. Some points such as during brownstock washing and effluent treatment seem to be prone to these types of problems. Many mills have been inundated by the shear volume of foam produced.

Extractives have been implicated in foaming problems during pulping, but it is recognized that many other factors contribute to this issue. In this phase of the study, several of these factors are explored in laboratory generated black liquors and TMP pressates that were generated from the mountain pine beetle-infested pines generated in the shelf life pulping studies conducted by Dalpke et al. [69].

### *3.2.1 Optimization of foaming conditions*

The apparatus described in the methods section was used to quantify foaming propensity as functions of both the amount of foam and its longevity. The amount of foam generated was quantified as the foam density, a dimensionless value calculated as the volume of liquid in a given volume of foam. The longevity of a foam was quantified as the collapse time, defined as the amount of time taken for a volume of foam to collapse completely into the liquid from which it was generated after the cessation of gas flow through that liquid. Together, foam density and collapse time are referred to as the foaming propensity of a given liquid. A liquid that has relatively high values for both foam density and collapse time, under specific conditions, has a high foaming propensity.

A matrix of trial conditions sought to optimize the three independent variables; temperature, $N_2$ flow rate and volume of liquor was applied to black liquor samples generated during the kraft pulping of red stage lodgepole pine samples. The standardized conditions were set at 45°C, 410 ml/min and 400 ml of liquor to be tested. These experiments also indicate the relative impact of these three factors on foaming propensity. Foam density was found to vary directly with gas flow alone, temperature had no significant effect on the amount or rate of foam generation (Figure 15). However, foam stability, as measured by collapse time, varied directly with gas flow but also varied inversely with temperature. Foam stability increased by 5 fold as liquid temperatures dropped from 60°C to 25°C (Figure 15). From a practical perspective, a mill should consider that foam stability increases dramatically as liquids cool.

### *3.2.2 The foaming of TMP pressates*

Pressates generated during the thermomechancial refining of lodgepole pines that were either green, red or grey were tested for foam generation and collapse times. Nine pressates were tested. The foam generation was too low to calculate an accurate foam density; therefore foam volumes are presented. Results of this study, presented in Figure 16, show that pressates produced during the refining of green or red stage pines produced little or no foams under the test conditions used (45°C, 410 ml/min of $N_2$ bubbled through 400 mls of unfiltered pressate). However, pressates produced during the refining of grey stage wood did show a marked increase in foaming. Similar increases in foam stability were also noted (foam volume generation was highly correlated with foam stability with the TMP pressates, $R^2 = 0.909$).

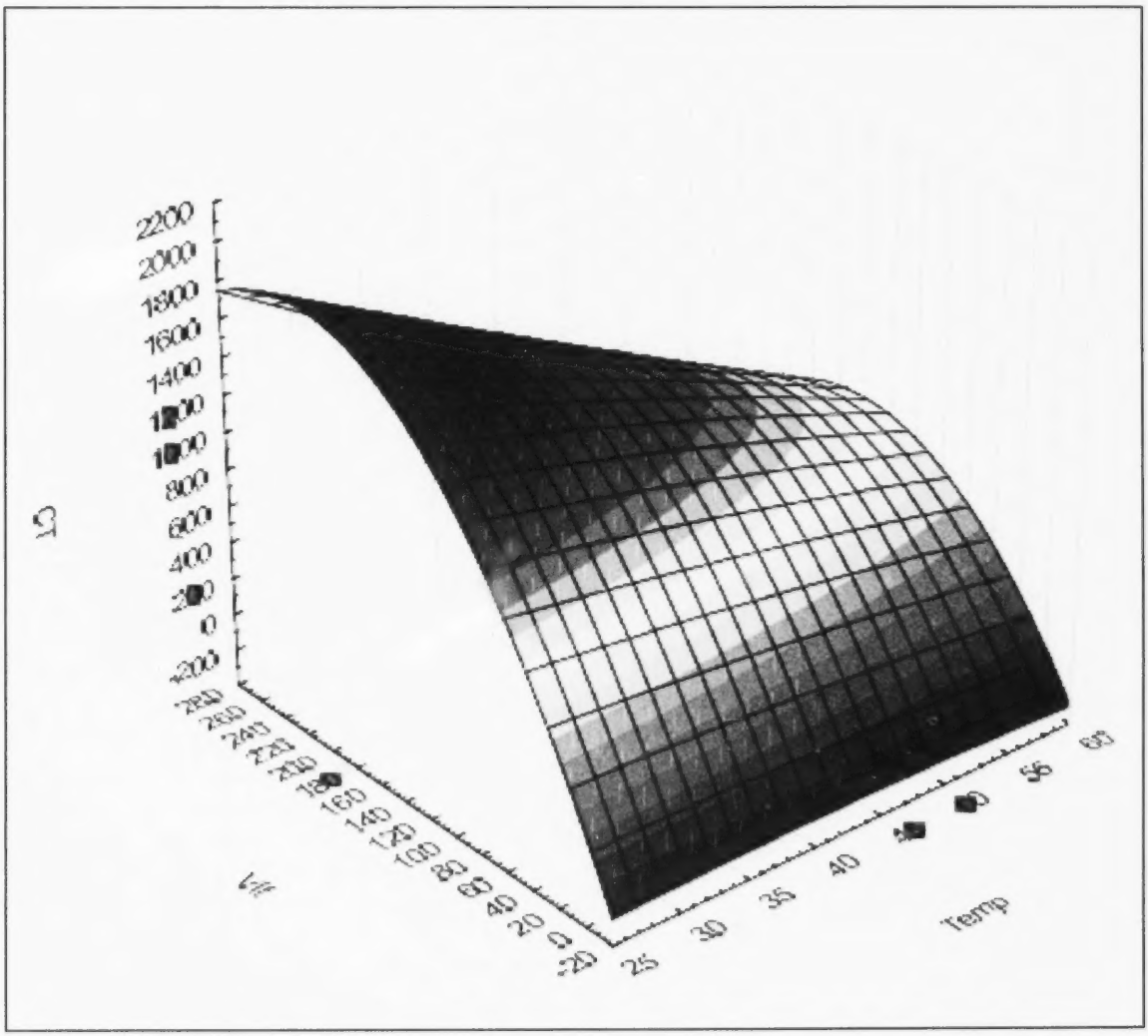


Figure 15. The effect of temperature (°C) and foam density (VIF) on collapse time (CT, in seconds). Note decrease in collapse time as temperature increases from 25°C to 60°C.

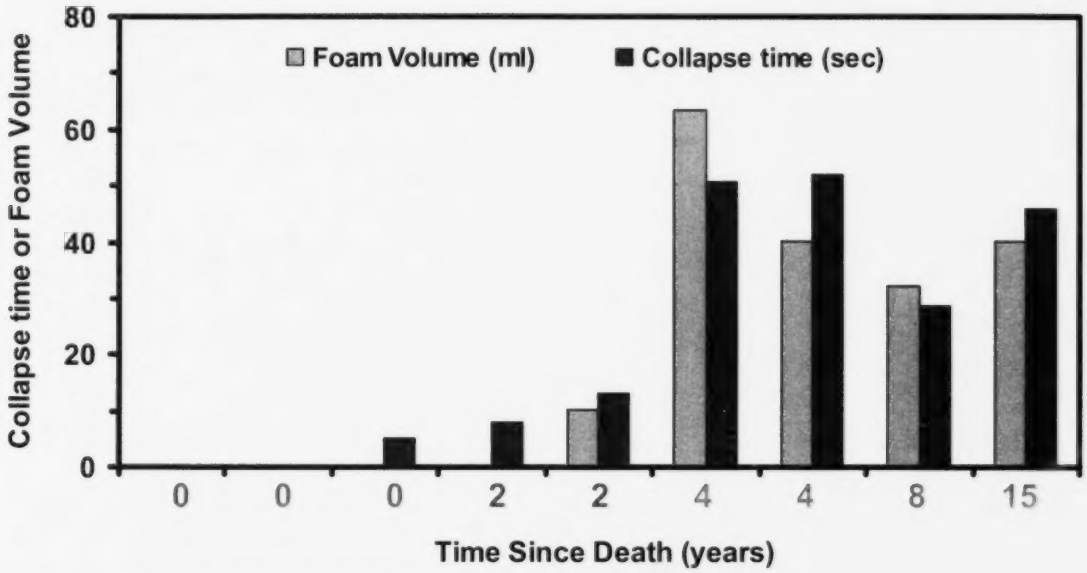


Figure 16. The foam volume (in ml) generated and collapse time (sec) of TMP pressates from the pilot scale thermomechancial refining of nine different lodgepole pines at different stages after mountain pine beetle infestation (unattacked-green, red, grey).

While a link between mountain pine beetle-affected wood and the foaming propensity of TMP pressates made from that wood is evident, whether this relationship is due to extractives levels in the pressate or to some other phenomenon needs to be explored. To determine the main effects of three factors on foam volume generation and collapse time, ANOVA was used; however no interactions between factors were considered (Table XIII). These factors were the extractives content of the pressates (expressed as % of solids), the solids content of the pressates, and the wood quality of the chips used in the refining (mountain pine beetle green, red or grey).

A comparison between the foam propensity parameters of the weak black liquors (Figure 18 and Figure 19) and the TMP pressates (Figure 16) readily shows that the black liquors produce more foams and more stable foams than the TMP pressates, under the same foam generating conditions. With the black liquors, true foam densities indicated that 10%-15% of the foam volume was liquid, while with the TMP pressates very low levels of liquid were incorporated into foams. Black liquor foams can be stable for up to 30 minutes or more, while TMP pressate foams collapse in about 1 minute. This is consistent with the view that the kraft pulping sector is more vulnerable to foam-related issues than the TMP sector. But excessive foaming is a problem for both sectors of the pulping industry and is highly dependent on the configuration of individual mills.

Table XIII. Averages (std. dev.) for extractives and solids content for TMP pressates, by mountain pine beetle stage. Analysis of Variance (ANOVA) to determine the main effects of the extractives content of nine TMP pressates, solids contents of the pressates and the wood quality of the chips that were pulped (green, red, grey) on foaming volume and collapse time. Factors have a statistically significant effect on the dependent variables if the p-value is less than 0.050 (Boldface text). MPB = mountain pine beetle

| | Unattacked-green | Red | Grey |
|---|---|---|---|
| % Extractives in pressates | 2.7 (0.8) | 4.2 (2.1) | 3.4 (1.2) |
| % Solids in pressates | 11.7 (2.9) | 25 (18.4) | 25.7 (10) |

| Dependent Variable: Foaming volume (ml) | | | $R^2$ 0.883 | |
|---|---|---|---|---|
| Factor | d.f. | Mean Square | F-ratio | p-value |
| Extractives content of pressate | 1 | 55.69 | 0.416 | 0.554 |
| Solids content of pressate | 1 | 19.7 | 0.147 | 0.721 |
| MPB stage of chips | 2 | 1291.3 | 9.660 | **0.029** |
| Error | 4 | 133.7 | | |
| Dependent Variable: | | Collapse time (sec) | $R^2$ 0.971 | |
| Factor | d.f. | Mean Square | F-ratio | p-value |
| Extractives content of pressate | 1 | 20.4 | 0.251 | 0.643 |
| Solids content of pressate | 1 | 50.8 | 0.635 | 0.470 |
| MPB stage of chips | 2 | 798.6 | 9.989 | **0.028** |
| Error | 4 | 79.9 | | |

The TMP pressates from the grey and red stage woods had higher extractives levels than those from unattacked green stage woods. These extractives levels correlated poorly with the overall solids content in the pressates. In this study, we have seen that unattacked green chips tend to have higher levels of glycerides and lower levels of sterols than red stage chips. These patterns are expected to translate into the extractives levels in the pressates. Studies have correlated free fatty acids with increased foaming in TMP pressates, while sterols are thought not to contribute to foaming [70]. The ANOVAs presented in Table XIII indicate that extractives and solids contents of the pressates did not affect foaming volume or stability. However, whether the wood was in an unattacked-green, red or grey state did have a strong influence on the foaming propensity of the TMP pressates. The mean foam volumes and the mean collapse times of grey stage wood are more than 40 times greater than those of the pressates made from green woods (Figure 17). Also, grey stage pressates have similar extractives levels as red stage pressates, yet the former produce significantly more foams than the latter. Factors other than extractives contents alone are contributing to the foaming propensity of the TMP pressates. These factors are linked to the mountain pine beetle stage of wood, and could be due to changes in wood chemistry.

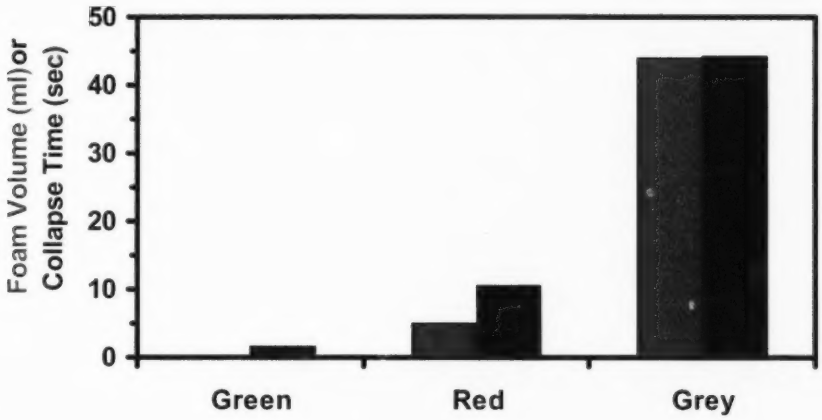


Figure 17. Mean foam volume (ml) and collapse time (sec) generated from the TMP pressates made from unattacked-green, red or grey stage lodgepole pine chips.

### *3.2.3 The foaming of kraft black liquors*

The same nine chip samples used in the TMP foaming experiments were also kraft pulped and the ensuing black liquors analyzed for the amount of foam generation (foam density) and foam stability (collapse time). The effects of mountain pine beetle-mediated changes to wood quality on foam density and foam collapse time are presented in Figures 18 and 19, respectively.

Figure 18. The foam density of weak black liquors from the pilot scale kraft pulping of 9 different lodgepole pines at different stages after mountain pine beetle infestation (unattacked-green, red, grey).

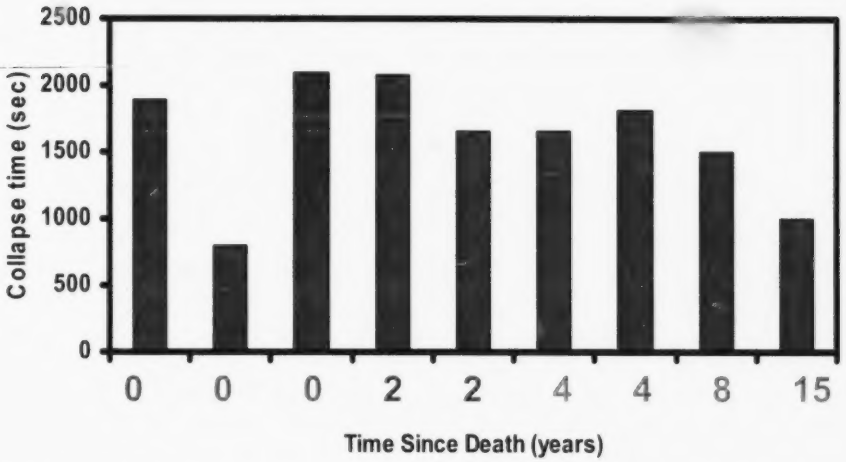


Figure 19. The collapse time (sec) of weak black liquors from the pilot scale kraft pulping of nine different lodgepole pines at different stages after mountain pine beetle infestation (unattacked-green, red, grey).

Weak black liquor samples were obtained from 23 different lodgepole pine chips samples that had been killed by mountain pine beetle and had been dead for different periods of time. These chips were kraft pulped under similar chemical charges (16% EA), but H-factors had been varied in order to generate pulps with kappa numbers close to 30. The foam density and collapse times of these weak black liquors were correlated with the green, red or grey stage status of the original chips. The ANOVA results indicated that there was no significant relationship between the amount of foam produced (foam density) and the mountain pine beetle status of the original wood. The mountain pine beetle state of the wood did have a statistically significant effect on foam stability (collapse time). However, the effect was relative small ($R^2$= 0.152, p-value >0.0001) and collapse times ranged between 25-30 minutes for the liquors made from the different types of wood. It would seem that any mountain pine beetle effects on foaming propensity could be affected by other factors, such as the physical properties of the black liquors.

Six properties associated with the weak black liquor were examined and their correlation coefficients with either foam density or collapse times are given in Table XIV. These black liquor properties were solids content, specific gravity, residual effective alkali, liquor viscosity and the total and lipophilic extractives content of the original chips. No significant correlations between any of the properties listed and foam density were noted (Table XIV). Two liquor properties, residual effective alkali and viscosity, were positively correlated and one, specific gravity, was negatively correlated with collapse time. Upon closer scrutiny, only viscosity was successfully regressed against collapse time, but this correlation, while significant, was weak ($R^2$= 0.239, p-value >0.001). It is postulated that the correlations between collapse time and specific gravity and REA were actually indirect, as these two properties also influence black liquor viscosity. Therefore, though some weak black liquor properties do affect foam stability, their relationship was not firmly established. This may be due to the narrow ranges in variation of some

properties, where greater variation could have strengthened some of the correlations. It would seem that, in order to establish whether mountain pine beetle is affecting the foaming propensity of weak black liquors, other strategies will be required.

Table XIV. Pearson correlation coefficients between five weak black liquor properties and either foam density or collapse time. Statistically significant coefficients ($\alpha<0.050$) are in boldface text.

| | Average | Range | Pearson Correlation Coefficient | |
|---|---|---|---|---|
| | | | Foam Density | Collapse time |
| Total extractives content of chips | 2.83 | 2.45 | 0.112 | -0.137 |
| Lipophilic extractives in chips | 1.37 | 1.05 | 0.266 | -0.306 |
| Solids content | 14.4 | 2.9 | 0.112 | -0.128 |
| Specific gravity | 1.075 | 0.012 | -0.495 | **-0.814** |
| Residual Effective Alkali | 5.1 | 3.1 | 0.604 | **0.800** |
| Viscosity | 1.168 | 0.136 | 0.384 | **0.857** |

One approach used to establish a link between mountain pine beetle-affected wood and the foaming propensity of the black liquors generated during the pulping of that wood, is to extract whole chips prior to kraft pulping and compare the foaming propensities of the liquors from the extracted chips with those of the liquors from the unextracted chips. This experiment was done on select red and grey stage chips, and the effects on foam densities and collapse times are presented in Figures 20 and 21, respectively. The results are expressed relative to the initial extractives contents of the chips prior to kraft pulping. This value is the extractives content of the unextracted chips, but not of the extracted chips which would be 60%-90% less than that of the unextracted.

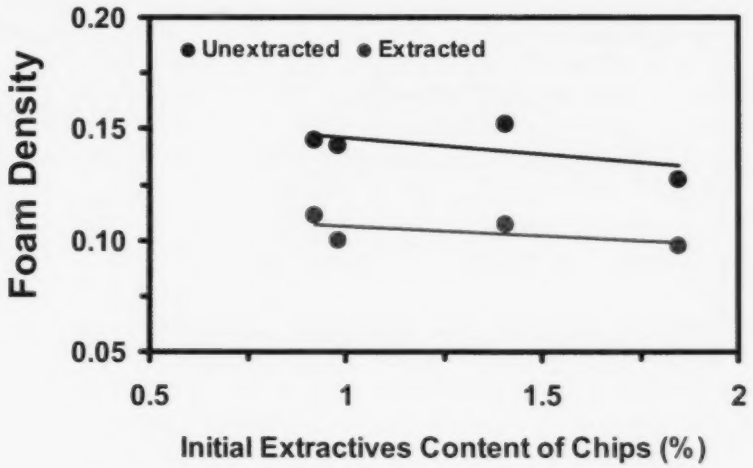


Figure 20. Effect of removing extractives on foam density of the ensuing weak black liquors.

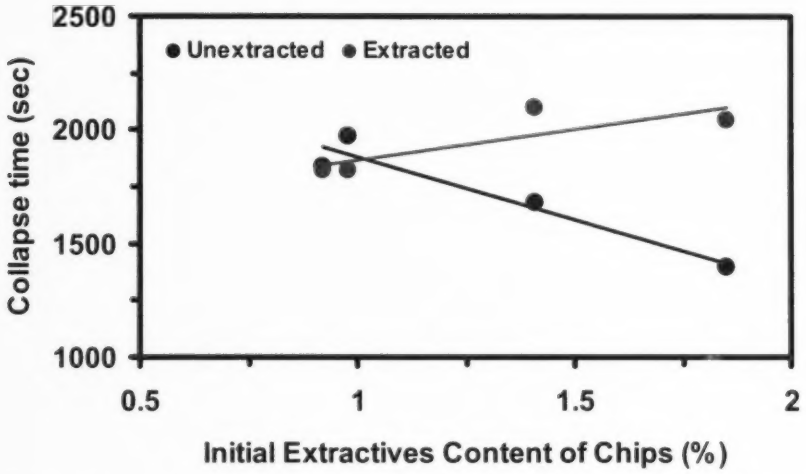


Figure 21. Effect of removing extractives on collapse time of foams from weak black liquors.

Weak black liquors from the kraft pulping of extracted pine chips generated, on average, 27% less foams than liquors from unextracted chips (Figure 20). The collapse time of foams generated from liquors made from unextracted chips decreased with initial extractives content. Collapse times of weak black liquors were over 12 minutes faster when the initial extractives content of the chips was 2% in contrast to chips with 1% extractives content (Figure 21). After chips were acetone extracted, the collapse time of the resulting weak black liquors remained consistent. This would suggest that extractives are acting as a de-foaming agent in these liquors.

To explore the effect of extractives on foam stability, extractives taken from grey stage chips were dissolved in acetone and added to weak black liquors generated during the pulping of the kraft pulping of extracted chips. The collapse times determined for the black liquors generated from the pulping of the unextracted, extracted no additives, and the extractives added are presented in Figure 22. In addition, the same volume of acetone (used in the "extractives added" trial) was added to an "extracted chips" black liquor, as a control.

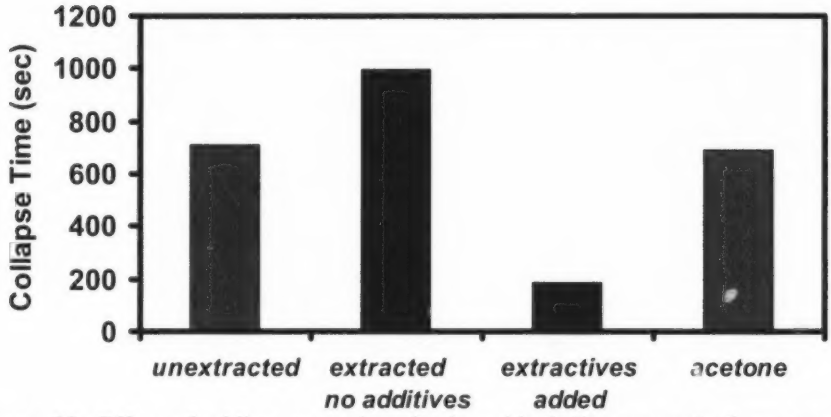


Figure 22. Effect of adding extractives back to black liquors made from extracted chips. The acetone served as a control. While all weak black liquors came from the same chip source, the red bar used liquors made from unextracted chips, the blue bars used liquors made from extracted chips.

The collapse times of the black liquors made from the unextracted chips were about 30% lower than that of liquors from the extracted chips (Figure 22), which is consistent with the results present in Figure 21 for chips with a 2% initial extractives content. When the extractives that were removed from the chips were added back to the liquors made from the extracted chips, the collapse time decreased by almost 5-fold. The impact of acetone alone, when added at the same charge as the "extractives added" experiment (50 ml of acetone to 400 ml of weak black liquor), was minor (ie, less than a 5% decrease in collapse time). The result of these experiments indicate that the presence of acetone extractives from grey stage wood act as de-foaming agents in weak black liquors by reducing foam stability.

The results of this experiment appear to contradict anecdotal evidence from mills that are reporting significant increases in foaming when using furnishes rich in red stage mountain pine beetle-infested pine. Reports in the literature indicate that fatty acid levels correlate positively with foaming [72], which would tend to suggest that liquors from red stage woods should foam less than those from unattacked green wood, based on levels noted in Table VIII. However, when the results presented in Table XIV are considered, it appears that many of the factors affecting weak black liquor foaming propensity are inherent properties such as viscosity or specific gravity. Properties such as residual effective alkali, which can influence liquor viscosity, also strongly influence foam stability. These appear not to be influenced by extractives, but may be affected by other wood chemistry attributes that could be influenced by beetle infestation or aging of wood. For example, as expected, viscosity has a large impact on foam stability (Table XIV). This liquor property is influenced by specific gravity, residual effective alkali and other chemical properties of the wood furnish being pulped, above and beyond extractives contents. It would appear that chemical attributes of the wood furnish, other than

extractives contents, are contributing to the foaming propensity of mountain pine beetle-killed pines.

## 4 Conclusions

The results presented in this study show that the extractives profiles of lodgepole pine trees killed by mountain pine beetle infestation are affected by a myriad of factors, not the least of which are site of growth and time-since-death post-beetle infestation. Partial Least Squares-Discriminant Analysis (PLS-DA) showed statistically significant differences in the extractives profiles of unattacked-green, red and grey stage lodgepole pines. The results show that red stage pine had lower levels of glycerides, but higher levels of sterols, than unattacked green wood. Grey stage woods had extractives profiles that are comparable to unattacked wood, likely due to the biodegradation of glycerides or to abiotic effects. However, these PLS-DA models were not robust enough to be used for classification of unknown pine samples into unattacked-green, red or grey stages of mountain pine beetle infestation. Resin acids, a major extractives class in pines, were unaffected by beetle infestation, although pimaric acid did tend to decrease with mountain pine beetle attack. Other approaches, possibly including the characterization of non-lipophilc compounds, may need to be explored to fully understand the implications of mountain pine beetle infestation on the extractives profiles of pines.

This study has demonstrated that, while extractives are implicated in the foaming tendency of TMP pressates and black liquors generated during the pulping of beetle-infested pine, other factors related to wood chemistry are just as important when addressing this issue. The chemical properties of mountain pine beetle-killed pines may contribute to the foaming propensity of TMP pressates. However, the effect of extractives contents of these wood furnishes on this phenomenon are minor. Similar conclusions were reached for weak black liquors using the same wood furnishes. This warrants further investigation into the nature of the chemical contributors to foaming propensity that can be linked to either mountain pine beetle infestation or the aging of dead, dry wood. By determining which chemical constituents are responsible for the foaming propensity of pulping liquors and waste streams, specific strategies can be developed that target the control of these compounds in situations prone to foaming.

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